

REDISTRIBUTION REACTIONS OF AMINE-BORANES  
WITH AMINE-HALOBORANES

By

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Dedicated to Joni

Thank you for your inexhaustible  
patience and understanding

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Abstract of Dissertation Presented to the  
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REDISTRIBUTION REACTIONS OF AMINE-BORANES  
WITH AMINE-HALOBORANES

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Major Department: Chemistry

Redistribution reactions between borane and haloborane adducts of amines are examined in hydrocarbon or halogenated hydrocarbon solvents. The reactions investigated include hydrogen-halogen and hydrogen-amine exchange. The hydrogen-halogen redistribution reactions studied include those between substituted pyridine-boryl and trimethylamine-boryl groups, and between two identical pyridine-boryl moieties. Hydrogen-amine exchange is investigated for the reaction of a substituted pyridine-borane with its monoiodinated derivative. Thus, for the adducts of pyridine donors, both types of exchange are observed in the same reaction system.

Equilibrium constants are determined for hydrogen-iodine exchange between substituted pyridine-boranes and trimethylamine-iodoboranes, and from them coordination enthal-

pies of a series of pyridine donors with iodoborane are ascertained. Based on the substituent effects on these coordination enthalpies, it is proposed that as an acceptor toward pyridine donors, iodoborane is sterically similar to borane, but electronically the iodoborane moiety contains a more positive boron atom and/or a more contracted acceptor orbital.

A kinetic study of the hydrogen-iodine exchange reaction indicates first order rate dependence with respect to each reactant. The rate of hydrogen-halogen redistribution is relatively insensitive to changes in the steric and electronic properties of the pyridine donor and ionic strength of the reaction medium, but increases sharply as the atomic weight of the halogen increases. The reaction is not catalyzed by free Lewis acid.

A mechanistic investigation of the hydrogen-iodine redistribution reaction demonstrates that the exchange process is not initiated by predissociation of a bond to boron to produce a trigonal species, but proceeds by the bimolecular reaction of coordinatively saturated amine-borane and amine-iodoborane adducts. A cyclic four-center transition state is advanced. Based on ultraviolet spectral data it is proposed that amine-iodoboranes may exist as intimate ion pairs in solvents of low dielectric constant. The ion pair model provides the unsaturation at boron required for facile four-center exchange.

The analysis of the hydrogen-halogen redistribution reactions is complicated by the occurrence of a secondary reaction formulated as the exchange of hydride on the pyridine-borane for a donor molecule of the pyridine-iodoborane to form ionic products, the dihydrobis(pyridine)boronium cation and the iodoborohydride anion. The anion is not isolated, presumably due to instability with respect to formation of diborane and iodide ion, which are obtained as products.

A kinetic study of the reaction leading to boronium cation formation reveals first order rate dependence with respect to each reactant and negative one-half order with respect to the product, diborane. Electron-donating substituents at the para position of the pyridine ring reduce the rate of reaction as do ortho alkyl substituents. In all cases examined, hydrogen-iodine exchange between two pyridine adducts is much faster than boronium cation production.

As with hydrogen-halogen redistribution, a dissociative mechanism for boronium cation formation is eliminated. The exchange process is initiated by the bimolecular reaction of coordinatively saturated amine-borane and amine-iodoborane. Nucleophilic displacement of a donor molecule from the pyridine-iodoborane by a boron-hydrogen bond of the pyridine-borane to form a bridged intermediate is proposed. Subsequent attack of the bridged species by the displaced amine yields the products. The inhibitive influence of diborane

is attributed to its complexation with the intermediary free amine.

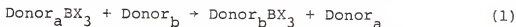
The utility of hydrogen-donor redistribution reactions for the preparation of bis(pyridine)boronium salts is demonstrated, and the optimum conditions for synthesis are discussed. The stabilities of boron Lewis acid adducts of amines with respect to bis(amine)boronium cation formation in general are interpreted in terms of the proposed mechanism.

The mechanisms of hydrogen-halogen and hydrogen-amine exchange are compared.

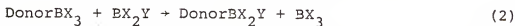


## CHAPTER I INTRODUCTION

Redistribution reactions in inorganic chemistry have received considerable attention in the last decade, and have been the subject of review articles, a conference, and a book.<sup>1-3</sup> As originally formulated by Skinner,<sup>4</sup> a redistribution reaction is one in which bonds change in relative positions, but not in numbers or types. In its loosest sense, this definition includes reactions of the type



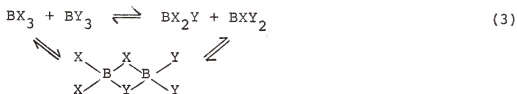
in which a Lewis base is displaced from its adduct with a boron Lewis acid by a second donor molecule. Van Wazer<sup>5</sup> has modified the Skinner definition by requiring that bonds be broken and formed to two or more central moieties during the course of the reaction. This more stringent definition, which will be adhered to herein, eliminates reactions analogous to 1 above from consideration as redistribution reactions. However, the displacement of a Lewis acid from its complex with a neutral donor by a second Lewis acid



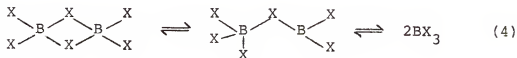
can be considered a redistribution reaction. Focusing on boron as a central atom, the reaction can be envisioned as the exchange of a B-X bond in the adduct for a B-Y bond in

the free acid, regardless of whether this interpretation is mechanistically correct.

The redistribution reactions of the Group III A elements, in particular boron, have received considerable attention. Especially notable are the exchange reactions of the coordinatively unsaturated trigonal boron compounds.



In monomeric three-coordinate boron compounds, the boron atom is  $\text{sp}^2$ -hybridized with a vacant  $2p$  orbital available for bond formation. Consequently, the boranes can form bridged dimers as intermediates of relatively low energy via the formation of three-center bonds. Likewise, dimeric boranes can undergo analogous exchange processes by predissociation into monomeric or singly bridged species.

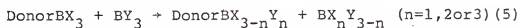


In either event, at least one unsaturated boron atom capable of bridge formation is liberated. Redistribution reactions of monomeric and dimeric boranes have been investigated for a variety of substituents on boron, and numerous kinetic and thermodynamic studies have been reported.<sup>1,3,6-8</sup>

Exchange reactions between a borane moiety and another

element as a central atom have been exploited synthetically, although few kinetic and thermodynamic data are available.<sup>1,9-13</sup>

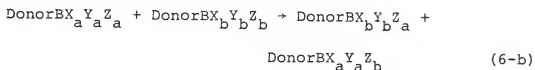
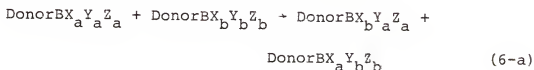
Redistribution reactions between a saturated four-coordinate boron atom in a donor-borane complex, and an unsaturated boron atom in a free Lewis acid have also been extensively investigated.<sup>7,12,14-23</sup>



This reaction scheme has been employed to prepare and study new donor-acceptor complexes, and considerable thermodynamic and mechanistic data are available. Isotopic labelling experiments have demonstrated that, for the strong donor trimethylamine, the boron-nitrogen dative bond remains intact during the exchange process.<sup>14</sup> An exchange process initiated by bridge bond formation to the unsaturated boron atom is consistent with the experimental data.

In contrast to the wealth of data reported for the redistribution reactions of systems containing unsaturated boron atoms, the exchange of substituents between two four-coordinate central boron atoms has received little attention. The scarcity of data in this area is not surprising since the tetrahedral boron atoms in these compounds are coordinatively saturated with no vacant orbitals available for bridge bond formation. The exchange of substituents between two saturated boron atoms in neutral donor-borane complexes can be classified into two general types. The first of these categories, which will be referred to as ligand-ligand ex-

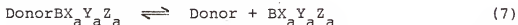
change, involves the redistribution of substituents in the acid portions of the donor-borane complexes.



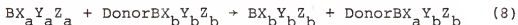
Donors employed have included ethers<sup>7,20</sup> dimethylsulfide,<sup>24</sup> esters,<sup>25</sup> phosphine,<sup>26,27</sup> triethylamine,<sup>28</sup> and N,N-dimethylaniline.<sup>29</sup> In all systems studied, the donor molecules in the two exchanging complexes were identical. No reports have been made of redistribution reactions between two complexes with different donor molecules. The other substituents on boron have included halogens and hydrogen, and in general, all three ligands in a given boron atom were identical. Although some equilibrium constants have been reported, no rate or mechanistic studies have been conducted.

The ability of two complexes to undergo exchange appears to have an inverse relationship with the strength of the donor-acceptor bond. Boron trihalide complexes of the strong donor, trimethylamine, fail to exchange halogens under conditions where the much weaker dimethylether adducts exchange readily.<sup>14,16,20</sup> Trimethylamine adducts undergo facile exchange only with uncomplexed boron trihalide. Consequently, it has been proposed that the exchange of substituents between two four-coordinate boron atoms can transpire only if dissociation to a trigonal boron atom occurs as a first step.

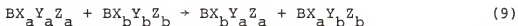
With the exception of triethylamine,\* all of the donor molecules studied to date are sufficiently weak bases toward the respective boron Lewis acids, that at room temperature a dissociative mechanism initiated by cleavage of the coordinate donor-borane bond is likely.



The Lewis acid so liberated would be free to exchange substituents with a molecule of donor-borane complex in a reaction analogous with equation 5,



or with another molecule of Lewis acid in a reaction analogous with equation 3.



In either event, redistributed Lewis acid could recombine with a donor molecule, and a scrambling of the substituents on the two tetrahedral boron atoms would result.

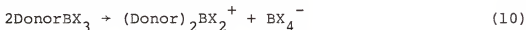
Miller<sup>14</sup> and Hartman<sup>13</sup> have concluded that the exchange of the substituents on boron in complexes with strong donors requires the presence of an unsaturated boron moiety in the system. Exchange between two saturated boron atoms can occur only if preceded by predissociation to a trigonal boron

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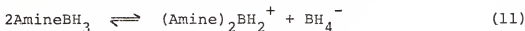
\*Although triethylamine is a strong donor toward boron Lewis acids, the exchange reactions reported by Faulks<sup>28</sup> were conducted at sufficiently high temperatures (100-120°C) that boron-nitrogen bond cleavage is expected. Coyle has demonstrated that significant boron-nitrogen bond cleavage occurs at 60°C for the triethylamine adducts of boron trifluoride and boron trichloride.<sup>18</sup>

species. The first evidence to the contrary is reported in this study. Facile exchange of ligands between saturated complexes of boron Lewis acids with strong donors such as trimethylamine and pyridine have been observed under non-dissociative conditions.

The second general category of redistribution reactions between four-coordinate boron atoms in neutral donor-borane complexes will be referred to as donor-ligand exchange. In this type of reaction a neutral donor molecule in one complex is exchanged for a negatively charged substituent in the acid portion of another molecule of complex, resulting in the formation of charged products.



Examples of this reaction are rare, and evidence for its operation has been presented only for pyridine,<sup>30</sup> piperidine,<sup>30</sup> acetonitrile,<sup>31-33</sup> and two aniline derivatives<sup>29</sup> as donors, all with halogen ligands on boron. In addition, Gillespie and Hartman have suggested that reaction 10 is a significant step in a reversible reaction sequence leading to the exchange of fluorine substituents between boron atoms in ketone adducts with boron trifluoride.<sup>15</sup> It has also been proposed that reversible donor-ligand exchange exists for ammonia and alkylamine adducts with  $\text{BH}_3$ .<sup>34</sup>



Whether this equilibrium actually exists has been the subject of considerable controversy in the literature.<sup>35-39</sup>

The latest results indicate that the tendency of the reaction to proceed in either direction at a given temperature is quite dependent on solvent (if any), and the presence or absence of trace impurities. Nevertheless, it is probably correct to state that the reaction has in fact been observed to occur in each direction in separate systems, although the question of facile equilibriums between amine-borane and salt has yet to be resolved.

No rate data for reaction 10 have been reported, and equilibrium data have been limited to the statement of Greenwood and Wade<sup>30</sup> that the reaction proceeds approximately 1% toward the ionic products in melts of the pyridine and piperidine adducts of boron trichloride. The present study reports the first kinetic and mechanistic investigation of a reaction formulated as donor-ligand exchange, and, as for ligand-ligand redistribution, a nondissociative reaction mechanism is proposed.

In summary, relatively little information has been reported for redistribution reactions between two four-coordinate boron atoms, with minimal thermodynamic data, and essentially no rate or mechanistic data available. The present study provides a detailed investigation of the kinetics and mechanisms of ligand-ligand exchange and donor-ligand exchange reactions in the same system, including redistribution between complexes of different donor molecules. Substituent exchange between saturated boron atoms via a non-dissociative mechanism is demonstrated for the first time.

Further, an equilibrium and thermodynamic study of ligand-ligand redistribution is presented. The results of the rate and equilibria studies have been combined with electronic spectral data to formulate a reaction path at tetrahedral boron that may have far-reaching implications.



## CHAPTER II

### MATERIALS, APPARATUS AND PROCEDURES

#### Materials

Pyridine-borane and trimethylamine-borane were obtained from Callery Chemical Company and were vacuum sublimed before use. Pyridine-borane was stored at  $-10^{\circ}\text{C}$ . Pyridine amines were obtained from Aldrich Chemical Company and were dried over calcium hydride and distilled before use. Cylinder gases were obtained from the Matheson Company and were used without further purification. Diborane was prepared by the method of Jolly,<sup>40</sup> and was purified immediately before use by several vacuum distillations through a  $-130^{\circ}\text{C}$  trap (n-pentane slush). Solvents used were reagent grade except for those employed in ultraviolet spectral studies, for which spectral grade solvents were used. Solvents were rigorously dried and distilled before use, discarding the first and last 10 % of the distillate. Hydrocarbon solvents and ethers were dried over calcium hydride or benzophenone and sodium-lead alloy, and chlorinated hydrocarbons were dried over phosphorus pentoxide. Except where noted, all other chemicals were commercially available and were reagent grade. When necessary they were dried before use by appropriate means.

### Apparatus and Procedures

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. Solid samples were prepared as KBr pellets, samples in solution were prepared in 0.1 mm cells with KBr windows, and gas samples were prepared in a 5 cm gas cell with NaCl windows. Spectra were referenced at  $1601\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  with polystyrene film. Intensities of absorptions are described as wk = weak, v wk = very weak, med = medium, and st = strong; and shapes of absorptions are described as s = sharp, br = broad, and sh = shoulder.

Proton nmr spectra were obtained at 60 MHz using a Varian Model A60-A spectrometer. Chemical shifts are reported in Hz, downfield from tetramethylsilane as an internal standard. A Varian V-6040 variable temperature controller was used to obtain low temperature spectra.  $^{11}\text{B}$  nmr spectra were obtained at 32.1 MHz using a Varian Model XL-100 spectrometer. Chemical shifts are reported in ppm, upfield from trimethylborate as an external standard.  $^{19}\text{F}$  nmr spectra were obtained at 94.1 MHz using a Varian Model XL-100 spectrometer, with chemical shifts reported in ppm, downfield from trifluoroacetic acid as an external standard.

Ultraviolet spectra were obtained using either a Cary 15 recording spectrophotometer or a Beckman DB-G grating spectrophotometer with 1 cm or 1 mm fused silica sample cells.

Melting points were recorded on a Thomas-Hoover apparatus and were uncorrected.

Constant temperature baths employed were the Poly-science-Haake Type FJ and the American Instrument Company Model Y 01-481.

The planimeter used was obtained from the American Industrial and Scientific Company, model # 13/83993.

Least squares calculations were performed using either a Wang 700 Series advanced programming calculator with linear regressions program no. 5643, sub-routine 0000, or a Wang 500 Series advanced programming calculator with linear regressions programs no. 2123 and 1882.

All procedures required for the preparation and handling of amine-haloborane solutions were performed in a Dri-Lab inert atmosphere chamber from Vacuum/Atmospheres Corporation. When it was necessary to cool kinetic samples below ambient temperature in the Dri-Lab, a Hoke Mini-Freezer Model PS 1 electric cooling unit was used. Stock amine-borane and amine-haloborane solutions were stored at  $-10^{\circ}\text{C}$  in tightly stoppered volumetric flasks in closed containers with Drierite desiccant.

Elemental analyses were performed by Peninsular Chem-Research, Incorporated, Gainesville, Florida, and Galbraith Laboratories, Incorporated, Knoxville, Tennessee.

## CHAPTER III EXPERIMENTAL AND RESULTS

### Kinetic and Thermodynamic Studies

#### Synthesis of Starting Materials

##### Synthesis of amine-boranes

Whereas pyridine-borane was commercially available for use in the rate and equilibrium studies it was necessary to prepare the substituted pyridine-boranes and deuterated amine-boranes by a variety of synthetic procedures. The products were all obtained as white crystalline solids except 2-t-butylpyridine-borane which melts near room temperature. Before use the solid materials were repeatedly recrystallized until melting points greater than or equal to literature values were obtained; 2-methylpyridine-borane was an exception.\*

Synthesis of 4-methylpyridine-borane. Trimethylamine-borane (41.65 g, 0.1571 mole) and 4-methylpyridine (85.0 ml, 0.860 mole, bp = 143.8-144.0°C at 756 mm) were dissolved in 300 ml of dry benzene and heated in an oil bath at 55-60°C

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\*Several recrystallizations of 2-methylpyridine-borane failed to reproduce the literature melting point. Several investigators in this laboratory have prepared and purified 2-methylpyridine-borane by a variety of methods, but none have been able to attain the literature value for the melting point, so that this value may be suspect.

for 19 hr. The volatile materials were removed under nitrogen flow and vacuum and the crude product was recrystallized from benzene by the addition of hexanes to give purified 4-methylpyridine-borane (40.09 g, 0.376 mole, 65.9% yield). The purified product had a melting point of 73.8-74.5°C (lit. 72-74°C<sup>41</sup>).

Synthesis of 2-methylpyridine-borane and 2,6-dimethylpyridine-borane. The free amines were distilled before use with 2-methylpyridine boiling at 128.0°C at 760 mm, and 2,6-dimethylpyridine boiling at 142.0°C at 758 mm. The amine-boranes were prepared by the method of Nainan and Ryschke-witsch<sup>42</sup> with a modification of the work-up procedure. The crude products were extracted with distilled water, filtered, and dried under vacuum before extraction with benzene and recrystallization by the addition of hexanes. Omission of the aqueous extraction resulted in a considerable amount of sodium iodide as an impurity in the recrystallized product. The melting points of the purified products were 46.6-47.0°C (lit. 50-51°C<sup>41</sup>) for 2-methylpyridine-borane and 110.5-111.5°C (lit. 110-111°C<sup>41</sup>) for 2,6-dimethylpyridine-borane.

Synthesis of 4-chloropyridine-borane. Sodium borohydride (13.63 g, 0.360 mole) was slurried with 600 ml of monoglyme and solid 4-chloropyridine hydrochloride (45.0 g, 0.300 mole) was added in portions over a 1 hr period. The mixture was slurried until gas evolution had stopped. The volatiles were then removed under nitrogen flow and vacuum. The residue was extracted with 900 ml of benzene and filtered.

Evaporation of the filtrate gave 34.38 g (0.270 mole, 90.0% yield) of crude product which melted at 115-125°C. After three recrystallizations from benzene by the addition of hexanes, a purified product melting at 136.5-137.5°C was obtained.

Synthesis of 2-*t*-butylpyridine-borane. The method of Nainan and Ryschkewitsch<sup>42</sup> failed to produce any significant yield of 2-*t*-butylpyridine-borane, presumably due to the inability of the hindered amine to compete favorably with the coordinating solvent (monoglyme) for borane. Instead, it was necessary to prepare the adduct by condensation of diborane onto the free amine on the vacuum line. Freshly purified diborane (0.00580 mole, 20% excess) was condensed at -196°C into a 50 ml round bottom flask containing 2-*t*-butylpyridine (0.00966 mole) which had been dried over calcium hydride and filtered before use. The mixture was allowed to warm to room temperature and was slurried. The condensation and warming processes were repeated until no more diborane was absorbed. The total amount of diborane absorbed (0.00457 mole) was 94.6% of the theoretical amount. The nmr spectrum of the crude product revealed the presence of an impurity which could not be removed by vacuum distillation. The integrated area of the impurity in the methyl region of the nmr spectrum was 9% of the total aliphatic area. The 2-*t*-butylpyridine-borane was used without further purification since the impurity was found to be unreactive in the systems studied. The melting point of the product

was 21-23°C (lit. 24-25°C<sup>41</sup>). Contrary to the report of Brown and Domash,<sup>41</sup> the 2-t-butylpyridine-borane was found to be unstable to air, decomposing rapidly with gas evolution on exposure to the atmosphere.

Synthesis of trimethylamine-borane-d<sub>3</sub>. Trimethylamine-borane-d<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>NBD<sub>3</sub>, was prepared from trimethylamine-borane, sulfuryl chloride, and deuterium oxide according to the method of Davis.<sup>43</sup> The procedure, which is reported to yield 98.1% deuteration on boron, was repeated three times to insure isotopic purity in excess of 99%.

Synthesis of 4-methylpyridine-borane-d<sub>3</sub>. 4-Methylpyridine-borane-d<sub>3</sub>, (4-CH<sub>3</sub>pyBD<sub>3</sub>), was prepared by the method described previously for 4-methylpyridine-borane substituting trimethylamine-borane-d<sub>3</sub> (see above) for trimethylamine-borane. The recrystallized product had a melting point of 73.0-74.8°C.

#### Synthesis of amine-haloboranes

The amine-haloboranes (R<sub>3</sub>NBH<sub>2</sub>X, X equal to halogen) used in the kinetic and thermodynamic studies were prepared from the amine-boranes described previously and a variety of halogenating agents according to established procedures.<sup>44,45</sup> In general, the amine-haloboranes were prepared in situ and were used without isolation. Stock solutions were stored in stoppered volumetric flasks kept in closed jars containing Drierite in a freezer at -10°C.

#### Equilibrium Constants for the Hydrogen-Halogen Exchange Reactions of Pyridine-Boranes with Trimethylamine-Haloboranes

The equilibrium constants (K<sub>eq</sub>) for the hydrogen-iodine

exchange reaction (reaction 37) were determined in methylene chloride at 35°C by integration of  $^1\text{H}$  nmr spectra of equilibrium mixtures. In general, equilibrium was approached by reacting the pyridine-borane derivative with trimethylamine-iodoborane. However, for 4-methylpyridine-borane, equilibrium was approached from both sides.

The reaction mixtures were prepared by the addition of an aliquot of amine-haloborane stock solution to a weighed amount of amine-borane or to an aliquot of amine-borane stock solution. Thus, the relative concentrations of the starting materials were known except for 2-t-butylpyridine-borane. In this case, the amine-borane contained an impurity, so the relative concentration of 2-t-butylpyridine-borane was determined by integration of the  $^1\text{H}$  nmr spectrum with trimethylamine-iodoborane as an internal standard.

The reaction mixtures were allowed to stand in stoppered test tubes for approximately 4-6 hr in the Dri-Lab inert atmosphere chamber at 35°C. Then samples of each solution were transferred to nmr tubes and nmr spectra were taken at 35°C. In each case, the spectrum contained resonances attributed to trimethylamine-borane and the iodinated pyridine-borane as well as those of the starting materials (see Figure 53 for 4-methylpyridine-borane). The spectral scans were repeated until no further change was observed in the 135 to 185 Hz region of the spectrum operating at a sweep width of 50 Hz over a 30 min period. Once equilibrium had been established, the spectrum of each sample was integrated at a 50 Hz



sweep width by means of a planimeter which had been demonstrated to be accurate and precise to within 0.5% of the measured areas. For the 4-chloro, 2-t-butyl, and unsubstituted pyridine derivatives, the relative concentrations of trimethylamine-borane and trimethylamine-iodoborane were obtained directly by integration of their respective signals at 156 Hz and 169 Hz. For the 4-methyl, 2-methyl, and 2,6-dimethylpyridine derivatives it was not possible to integrate both the trimethylamine-borane and trimethylamine-iodoborane peaks due to the overlap of one of these with a pyridine methyl resonance. However, in each case it was possible to integrate either the trimethylamine-borane or trimethylamine-iodoborane area vs. the total aliphatic area (135 to 185 Hz). Then simple calculations based on the known stoichiometry of the system provided the relative integral areas of the trimethylamine-borane and trimethylamine-iodoborane resonances. Although absolute concentrations of the solutes were not generally known precisely, their relative concentrations could be determined directly from their relative integral areas. Calculations of equilibrium constants require only that the relative concentrations of the solutes in the equilibrium expression are known.

For each equilibrium system, it was necessary to apportion the total aliphatic area into components representing one or more of the solutes by extrapolation of partially resolved peaks into regions of overlapping resonances. In

so doing, it was necessary to construct several such apportionments for each sample in order to establish error limits for the integrated areas and ultimately for the equilibrium concentrations. An example of this treatment is presented in more detail in the appendix for the 4-chloropyridine-borane system.

In addition to the methyl resonances of the trimethylamine and methylpyridine moieties, the area of interest in the aliphatic region of each nmr spectrum also contained a broad signal centered near 150 Hz attributable to a boron-bonded hydrogen. This resonance represents one portion of a 1:1:1:1 quartet due to the hydrogens bonded to the  $^{11}\text{B}$  isotope in trimethylamine-borane. The isotopic abundance of the  $^{11}\text{B}$  isotope is 81.1% so that the methyl component of a trimethylamine-borane signal containing one portion of the  $^{11}\text{B}$ -H quartet is given by:

$$\begin{aligned}
 (\text{CH}_3)_3\text{NBH}_3(\text{CH}_3) &= \text{total } (\text{CH}_3)_3\text{NBH}_3 \text{ area} \\
 &\quad \times \frac{9.00}{9.00 + (3.00)(0.250)(.811)} \\
 &= 0.937 \text{ total } (\text{CH}_3)_3\text{NBH}_3 \text{ area} \quad (12)
 \end{aligned}$$

Thus, it was necessary to multiply trimethylamine-borane integrals by 0.937 before calculating the relative concentrations of trimethylamine-borane and trimethylamine-iodoborane. There is a minimal degree of uncertainty in this treatment due to the broadness of the boron-hydrogen resonance. A small portion of this peak could overlap with the trimethylamine-iodoborane signal.

The relative concentrations of the pyridine-boranes and the pyridine-iodoboranes could not generally be obtained directly by integration of the nmr resonances due to the poor resolution of their signals. However, the relative concentrations of these materials could be determined indirectly from the concentrations of trimethylamine-borane and trimethylamine-iodoborane at equilibrium, the initial concentrations of the starting materials, and the stoichiometry in equation 37, taking into consideration the effects of side reactions. In the absence of any side reactions the equilibrium concentrations of the pyridine-iodoborane and the pyridine-borane would be given by

$$[\text{R-pyBH}_2\text{I}]_e = [(\text{CH}_3)_3\text{NBH}_3]_e \quad (13)$$

and

$$[\text{R-pyBH}_3]_e = [\text{R-pyBH}_3]_o - [(\text{CH}_3)_3\text{NBH}_3]_e \quad (14)$$

where subscripts o and e denote initial and equilibrium concentrations, respectively. However, in the presence of any side reactions equations 13 and 14 are not valid and must be adjusted according to the stoichiometry and extent of the side reaction. In nearly all systems studied a side reaction between the pyridine-borane and the pyridine-iodoborane occurred to produce diborane and dihydrobis(pyridine)boronium iodide,  $(\text{R-py})_2\text{BH}_2^+\text{I}^-$ , according to equation 43. Then equations 13 and 14 must be replaced by

$$[\text{R-pyBH}_2\text{I}]_e = [(\text{CH}_3)_3\text{NBH}_3]_e - [(\text{R-py})_2\text{BH}_2^+]_e \quad (15)$$

and

$$[\text{R-pyBH}_3]_e = [\text{R-pyBH}_3]_o - [(\text{CH}_3)_3\text{NBH}_3]_e - [(\text{R-py})_2\text{BH}_2^+]_e \quad (16)$$

For each system examined, a sufficiently accurate estimate of the extent of reaction 43 could be made by nmr integration as described in a later section. Consequently the concentration of the bis(pyridine)boronium iodide, and finally the concentrations of the pyridine-borane and pyridine-iodoborane, could be determined by equations 15 and 16 in the absence of any other side reactions. For some derivatives another side reaction was observed, so that refinements of equations 15 and 16 were necessary. For the 4-methyl, 4-chloro, and unsubstituted pyridine derivatives, another minor side reaction occurred to produce a product absorbing at 164 Hz in the nmr spectrum. It was not known whether this peak resulted from a side reaction of trimethylamine-borane or trimethylamine-iodoborane so it was necessary to consider both possibilities when determining the error limits for the pyridine-borane and the pyridine-haloborane concentrations. In so doing, it was necessary to modify equations 15 and 16 to include the effects of this side reaction

$$[\text{R-pyBH}_2\text{X}]_e = [(\text{CH}_3)_3\text{NBH}_3]_e - [(\text{R-py})_2\text{BH}_2^+]_e + [164]_e \quad (17)$$

and

$$[\text{R-pyBH}_3]_e = [\text{R-pyBH}_3]_o - [(\text{CH}_3)_3\text{NBH}_3]_e - [(\text{R-py})_2\text{BH}_2^+]_e + [164]_e \quad (18)$$

where  $[164]_e$  represents the equilibrium concentrations of trimethylamine groups in the unassigned product at 164 Hz.

By means of equations 13 through 18 the equilibrium concentrations of the pyridine-boranes and the pyridine-iodoboranes were determined and recorded in Table 1. Finally the equilibrium constants in Table 1 were calculated according to equation 46 from the equilibrium concentrations of the amine-boranes and amine-iodoboranes. The error limits assigned to the equilibrium constants are based on maximum additive effects of the uncertainties in the equilibrium concentrations of the solutes. The errors in the equilibrium concentrations of the solutes reflect all sources of uncertainty mentioned previously; i.e.:

- (a) Uncertainty in the resolution of the total aliphatic spectrum into its components.
- (b) Uncertainty of the origin of the unassigned peak at 164 Hz.
- (c) Uncertainty in the equilibrium concentrations of the pyridine-borane and the pyridine-haloborane due to the error in the determination of the extent of side reaction 43.
- (d) Uncertainty in the relative sizes of the trimethylamine-borane and trimethylamine-haloborane integral areas due to the resonance of boron-hydrogens.

These effects are listed in decreasing order of their significance, with the influence of the first factor generally the dominant source of error. More detail of the error

Table 1  
Equilibrium Data for the Hydrogen-Halogen Exchange Reactions  
of Pyridine-Boranes and Trimethylamine-Haloboranes

X	R in R-py	Temp. °C	$[(CH_3)_3NBH_3]_e^a$	$[(CH_3)_3NBH_2X]_e^a$	$[R-pyBH_2X]_e^a$
I	H	35	.576 $\pm$ .005	.413 $\pm$ .005	.460 $\pm$ .023
I	4-Cl	35	.526 $\pm$ .005	.473 $\pm$ .005	.377 $\pm$ .010
I	4-CH <sub>3</sub>	35	.636 $\pm$ .006	.348 $\pm$ .006	.539 $\pm$ .019
I <sup>d</sup>	4-CH <sub>3</sub>	35	.640 $\pm$ .006	.344 $\pm$ .006	.543 $\pm$ .019
I	4-CH <sub>3</sub>	0	.681 $\pm$ .006	.319 $\pm$ .006	.651 $\pm$ .012
I <sup>e</sup>	4-CH <sub>3</sub>	0	.689 $\pm$ .006	.311 $\pm$ .006	.689 $\pm$ .012
I <sup>f</sup>	4-CH <sub>3</sub>	35	.640 $\pm$ .006	.342 $\pm$ .006	.539 $\pm$ .020
I	2-CH <sub>3</sub>	35	.563 $\pm$ .006	.437 $\pm$ .006	.463 $\pm$ .021
I	2,6-(CH <sub>3</sub> ) <sub>2</sub>	35	.640 $\pm$ .013	.354 $\pm$ .013	.606 $\pm$ .022
I	2-(CH <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	35	.497 $\pm$ .007	.503 $\pm$ .007	.417 $\pm$ .015
Br <sup>g</sup>	4-CH <sub>3</sub>	24	.515 $\pm$ .022	.485 $\pm$ .022	.445 $\pm$ .095
Br <sup>g</sup>	4-CH <sub>3</sub>	24	.514 $\pm$ .019	.486 $\pm$ .019	.404 $\pm$ .056
Cl <sup>h</sup>	4-CH <sub>3</sub>	24			
Cl <sup>h</sup>	4-CH <sub>3</sub>	24			

<sup>a</sup> Concentrations were normalized to a total concentration of trimethylamine groups of 1.000 M.

<sup>b</sup> [164]<sub>e</sub> denotes the concentration of trimethylamine groups in a side product of unknown origin.

<sup>c</sup> None detected.

<sup>d</sup> Equilibrium was attained by the reaction of the pyridine-haloborane and trimethylamine-borane.

<sup>e</sup> The nmr tube also contained a pressure of diborane.

<sup>f</sup> The boron hydrogens were substituted with deuterium.

<sup>g</sup> Equilibrium had not been attained, but was approached from both sides to establish a range for  $K_{eq}$ . The values reported above for  $K_{eq}$  are Q values where  $Q = [R-pyBH_2X][ (CH_3)_3NBH_3 ] / [R-pyBH_3][ (CH_3)_3NBH_2X ]$ . The concentrations were determined at a point near equilibrium.

<sup>h</sup> An attempt was made to approach equilibrium from either side but no exchange was detected after 20 days at 26 $\pm$ 2°C.

Table 1 - Extended

$[\text{R-py}^3\text{H}_3]_e^a$	$[(\text{R-py})_2\text{BH}_2^+\text{X}^-]_e$	$[\text{164}]_e^{a,b}$	$K_{eq}$
.296 $\pm$ .023	.122 $\pm$ .012	.011	2.18 $\pm$ .20
.324 $\pm$ .010	.149 $\pm$ .004	.001	1.29 $\pm$ .07
.251 $\pm$ .019	.105 $\pm$ .005	.016	3.96 $\pm$ .47
.247 $\pm$ .019	.100 $\pm$ .005	.016	4.12 $\pm$ .45
.305 $\pm$ .012	.022 $\pm$ .005	c	4.57 $\pm$ .39
.311 $\pm$ .012	c	c	4.93 $\pm$ .41
.241 $\pm$ .020	.110 $\pm$ .005	.018	4.23 $\pm$ .54
.337 $\pm$ .021	.100 $\pm$ .015	c	1.78 $\pm$ .11
.315 $\pm$ .022	.039 $\pm$ .009	c	3.56 $\pm$ .48
.220 $\pm$ .015	.080 $\pm$ .008	c	1.89 $\pm$ .18
.318 $\pm$ .016	.071 $\pm$ .005	c	1.58 $\pm$ .50
.419 $\pm$ .020	.079 $\pm$ .005	c	1.00 $\pm$ .31

analysis including a sample calculation can be found in the appendix.

In summary, the equilibrium constants for reaction 37 for each derivative were determined by the following sequence of steps:

- [1] After 4-6 hr at 35°C the nmr spectrum of each sample was repeatedly taken at 35°C until no further change was observed over a 1/2 hr period in the 135 to 185 Hz region operating at a 50 Hz sweep width.
- [2] The final spectrum was apportioned several times into its component areas by extrapolation of partially resolved peaks into regions of overlap.  
(See Figure 63 and the related discussion in the appendix).
- [3] Each apportionment of the spectrum was integrated with a planimeter to determine the relative areas of the resonances of trimethylamine-borane, trimethylamine-iodoborane, and the unassigned peak at 164 Hz.
- [4] The trimethylamine-borane area was compensated for boron-hydrogen resonance, according to equation 12.
- [5] Concentration ranges for trimethylamine-borane and trimethylamine-iodoborane at equilibrium were calculated considering the influences of the errors in steps 2 and 4.
- [6] The concentration of  $(R-py)_2BH_2^+X^-$  was determined

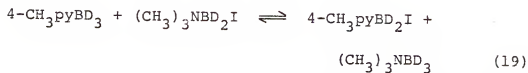


by nmr integration.

- [7] Concentration ranges for the pyridine-borane and the pyridine-iodoborane were determined using equations 13 through 18.
- [8] A range for the equilibrium constant was calculated from equation 46. The error limits given in Table 1 for  $K_{eq}$  are based on maximum additive effects of the concentration errors.
- [9] Steps 1 and 6 were repeated for a duplicate sample. For each derivative, duplicate samples exhibited essentially identical nmr spectra.

In a similar manner, the equilibrium constant for the 4-methylpyridine-borane derivative was determined approaching equilibrium from the right side of equation 37 as written. The procedure was the same as described above except that equations 17 and 18 had to be somewhat modified before calculating the equilibrium concentrations of 4-methylpyridine-borane and 4-methylpyridine-iodoborane.

Likewise, the equilibrium constant for deuterium-iodine exchange between 4-methylpyridine-borane- $d_3$  and trimethylamine-iodoborane- $d_2$  was determined in methylene chloride at 35°C.

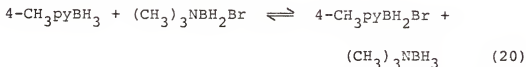


The procedure was the same as that outlined for hydrogen-iodine exchange, except that step 4 in the method could be

omitted since there were no boron-hydrogen resonances.

The equilibrium constant for 4-methylpyridine-borane was also determined at 0°C by a slightly modified procedure. The reaction mixture containing 4-methylpyridine-borane and trimethylamine-iodoborane in methylene chloride was kept at 0°C for 70 hr. After this time had elapsed, equilibrium had been attained, and the nmr spectrum was taken at 0°C. At this temperature, the downfield aromatic resonances of 4-methylpyridine-borane and 4-methylpyridine-iodoborane were sufficiently resolved to allow the determination of the relative concentrations of these solutes by direct integration rather than by use of equations 17 and 18. Likewise, the equilibrium constant for the exchange reaction between 4-methylpyridine-borane and trimethylamine-iodoborane under a pressure of approximately 1 atm of diborane (cf page 66) was determined at 0°C.

The exchange reaction was also investigated for other halogens in addition to iodine. The exchange of hydrogen for bromine between trimethylamine-boryl and 4-methylpyridine-boryl moieties in methylene chloride was examined from both sides of the equilibrium.



A solution containing 4-methylpyridine-borane (1.0 M) and trimethylamine-bromoborane (1.0 M) was allowed to stand at room temperature ( $24 \pm 2^\circ\text{C}$ ) for several weeks in a capped

nmr tube. Likewise, a solution containing 4-methylpyridine-bromoborane (1.0 M) and trimethylamine-borane (1.0 M) was allowed to stand under the same conditions.  $^1\text{H}$  nmr spectra of each solution were taken periodically, and after approximately 40 days neither system had come to equilibrium with respect to reaction 20. However, a range for the equilibrium constant could be determined by the calculation of Q values for the approach to equilibrium from each side where

$$Q = \frac{[4\text{-CH}_3\text{pyBH}_2\text{Br}][(\text{CH}_3)_3\text{NBH}_3]}{[4\text{-CH}_3\text{pyBH}_3][(\text{CH}_3)_3\text{NBH}_2\text{Br}]} \quad (21)$$

Q values for the two amine-borane/amine-bromoborane systems at various times after mixing are recorded in Table 2. Adequate resolution of the upfield aromatic resonances in the nmr spectra allowed integration of the 4-methylpyridine-borane and 4-methylpyridine-bromoborane signals, so that their relative concentrations could be determined directly rather than by use of equations analogous to 17 and 18. The relative concentrations of trimethylamine-borane and trimethylamine-bromoborane were determined by integration of the aliphatic region of the nmr spectrum as described previously for hydrogen-iodine exchange reactions. A side reaction analogous to equation 43 occurred producing bis-(4-methylpyridine)boronium bromide. In addition, another side reaction, which appeared to be solvolysis, was detectable in the nmr spectrum. On long standing (15-20 days) a small very sharp singlet appeared 7 Hz upfield from the

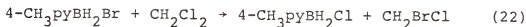
Table 2  
Q Values for Hydrogen-Bromine Exchange

Reagents <sup>a, b</sup>	Time	Q
4-CH <sub>3</sub> pyBH <sub>3</sub> + (CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> Br	0	0
	10 days	0.095
	20 days	0.352
	43 days	1.00
4-CH <sub>3</sub> pyBH <sub>2</sub> Br + (CH <sub>3</sub> ) <sub>3</sub> NBH <sub>3</sub>	0	∞
	5 days	19.3
	15 days	5.16
	38 days	1.58

<sup>a</sup> The initial concentration of each reagent was approximately 1.0 M

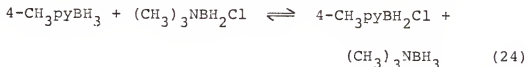
<sup>b</sup> In methylene chloride at 24±2°C

solvent peak. The shape and position of this peak suggested that it was a resonance of bromochloromethane.<sup>13</sup> Since no trimethylamine-chloroborane could be detected, it is expected that the bromochloromethane was a product of a reaction of the solvent either with 4-methylpyridine-bromoborane (reaction 22), or with the bromide counter ion of the bis-(4-methylpyridine)boronium cation,  $(4\text{-CH}_3\text{py})_2\text{BH}_2^+$ , (reaction 23).



Based on the  $^1\text{H}$  nmr spectrum of the reaction mixture, it was not possible to deduce which of these two reactions had occurred, but the observed rate of bromochloromethane production was similar to the reported rate of reaction 23.<sup>13</sup> The ranges given in Table 1 for the solute concentrations and Q reflect the uncertainty introduced by the solvolysis reaction as well as some of the other sources of error discussed previously for the hydrogen-iodine exchange reactions.

Attempts to determine an equilibrium constant for hydrogen-chlorine exchange between trimethylamine-boryl and 4-methylpyridine-boryl moieties were unsuccessful.



Approach to equilibrium was attempted from each side, but even concentrated solutions (0.5-1.0 M) failed to produce any detectable exchanges on standing for 20 days at room

temperature ( $24 \pm 2^\circ\text{C}$ ) in methylene chloride. It was estimated that the nmr spectra would have been sensitive to approximately 1% net reaction in either direction, but none was detected.

Kinetics of the Hydrogen-Halogen Exchange Reaction of Pyridine-Boranes with Trimethylamine-Haloboranes

Hydrogen-iodine exchange

The initial rates of hydrogen-iodine exchange reaction 52 were measured at  $35^\circ\text{C}$  in methylene chloride for R equal to H, 4-Cl, 4- $\text{CH}_3$ , 2- $\text{CH}_3$ , 2,6- $(\text{CH}_3)_2$ , and 2- $\text{C}(\text{CH}_3)_3$ . The progress of the reaction was monitored by integration of the 140 Hz to 180 Hz region in the nmr spectrum as a function of time. The integral area attributed to trimethylamine-borane ( $\delta = 156$  Hz) was adjusted according to equation 12 to eliminate the contributions due to the resonance of boron-hydrogens. The adjusted integral area of the trimethylamine-borane peak vs. the total trimethylamine area provided a determination of the concentration of trimethylamine-borane at each time (t) according to

$$[(\text{CH}_3)_3\text{NBH}_3] = \frac{0.937 + A}{0.937 A + B} \times [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 \quad (25)$$

where A is the total integrated trimethylamine-borane area, and B is the integrated trimethylamine-iodoborane area.

For the unsubstituted pyridine derivative several trimethylamine-borane concentrations vs. time plots were constructed for various initial concentrations of the reagents, and the slopes (V) of tangents at  $[(\text{CH}_3)_3\text{NBH}_3] = 0.050$  were

measured (Figures 1 - 7). Table 3 summarizes the concentration and slope data for these runs. Log-log plots of the slopes of these tangents vs. concentration allowed the determination of the order of reaction 52 with respect to each reagent (Figures 8 and 9). The least squares slopes of Figures 8 and 9 demonstrated that reaction 52 was first order in each reagent. Plots of the appropriate integrated second order rate expression vs. time allowed the determination of a value for the second order rate constant ( $k_2$ ) for each run (Figures 10 - 16). In these and subsequent plots,  $x$  is the molar concentration of trimethylamine-borane at time  $t$ ,  $a_0$  is the initial molar concentration of the pyridine-borane, and  $b_0$  is the initial molar concentration of trimethylamine-iodoborane. For each run, the value determined for the second order rate constant was the slope of the least squares fit of the linear plot. Likewise, least squares plots and second order rate constants were determined for several runs with various concentrations of tetra- $n$ -butylammonium iodide,  $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{I}^-$  (Figures 17 - 19). The results for all runs for pyridine-borane are summarized in Table 4. Plots of the appropriate integrated second order rate law vs. time were also constructed for the other pyridine-boranes, and the least squares slopes determined (Figures 20 - 29). The results for the substituted pyridine derivatives are summarized in Table 5. Table 6 lists the average of  $k_2$  at 35°C for the seven runs for pyridine-borane, and for each set of duplicate runs for the substituted pyri-

and pbs

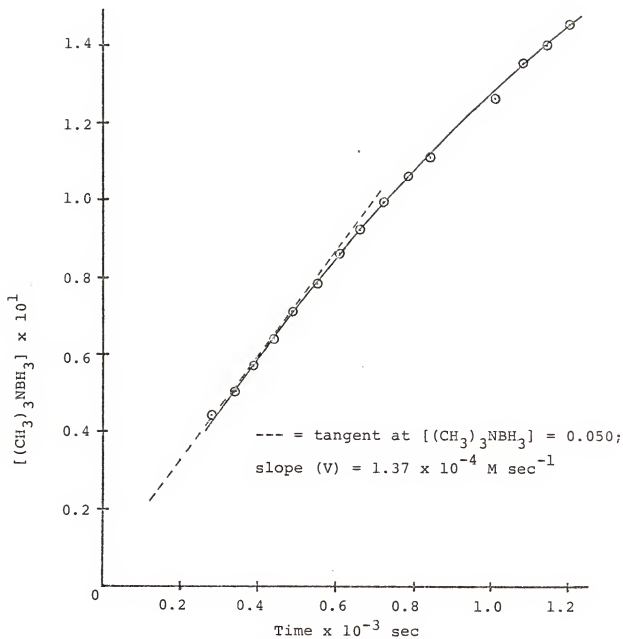


Figure 1. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.500$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .



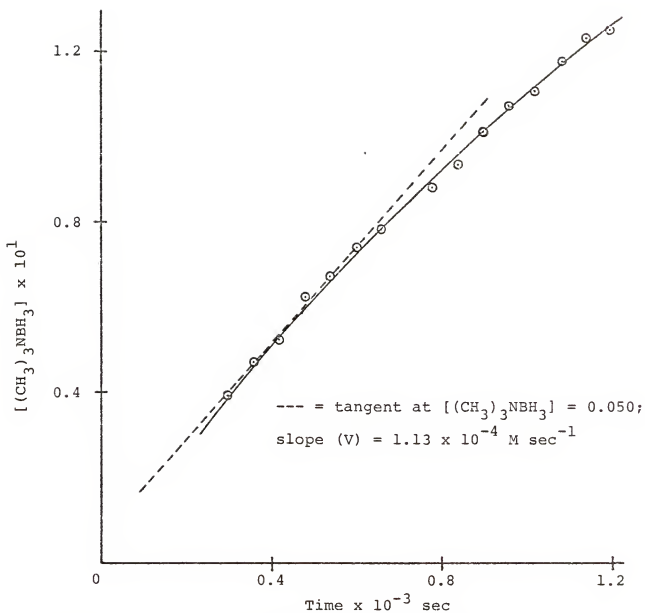


Figure 2. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.400$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

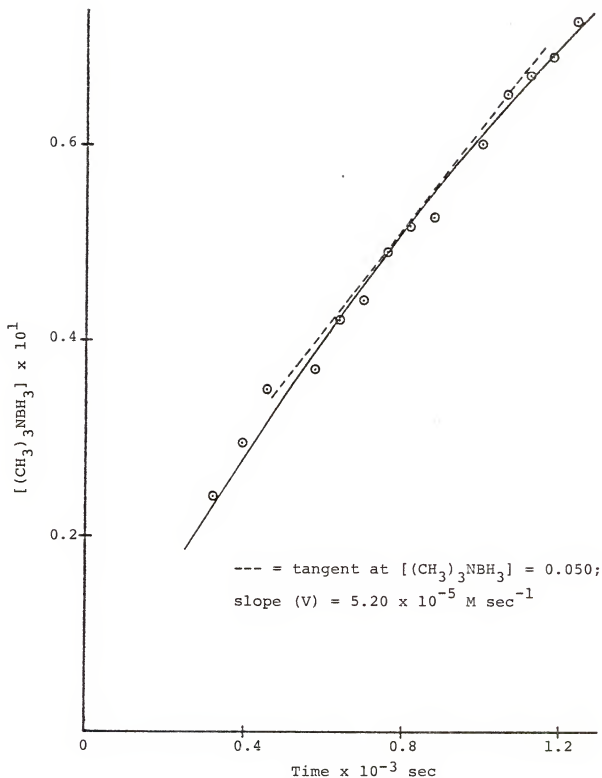


Figure 3. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.220$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

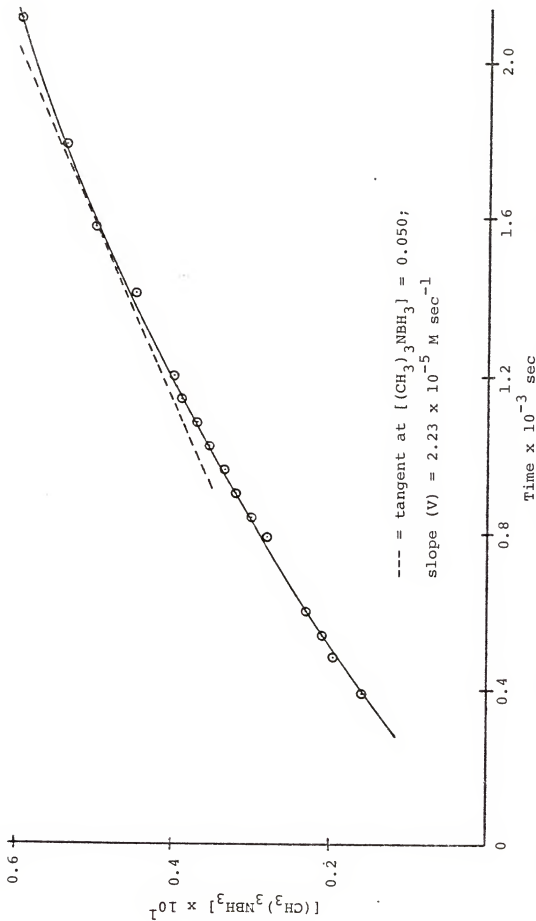


Figure 4. Trimethylamine-borane concentration vs. time plot (—) for  $[\text{pyBH}_3]_0 = 0.125$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

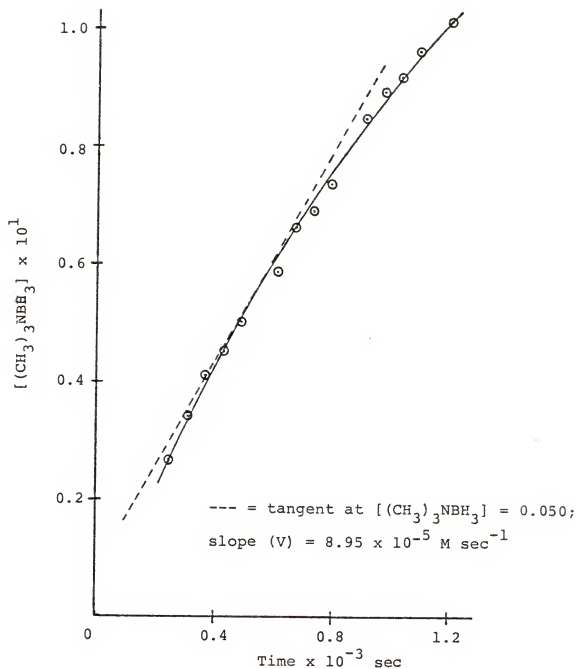


Figure 5. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.500$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.370$ .

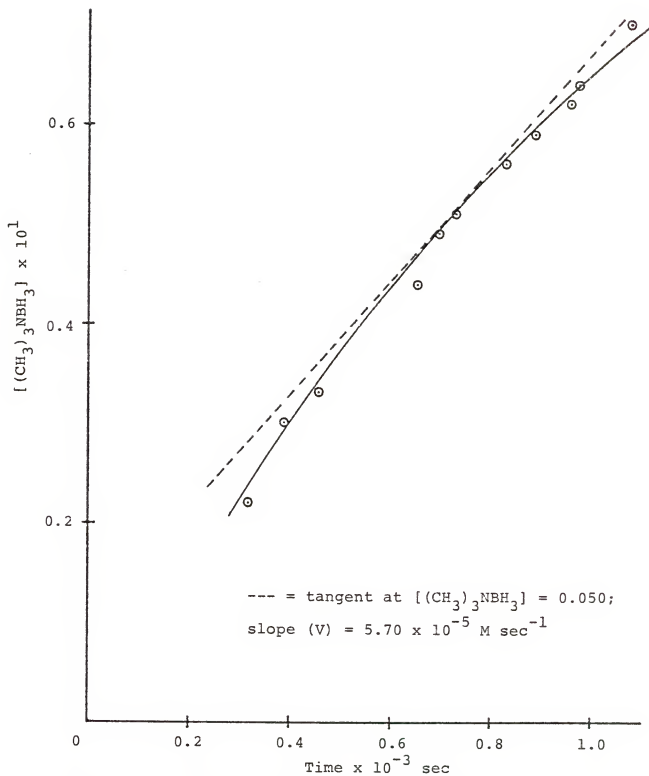


Figure 6. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.500$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.250$ .

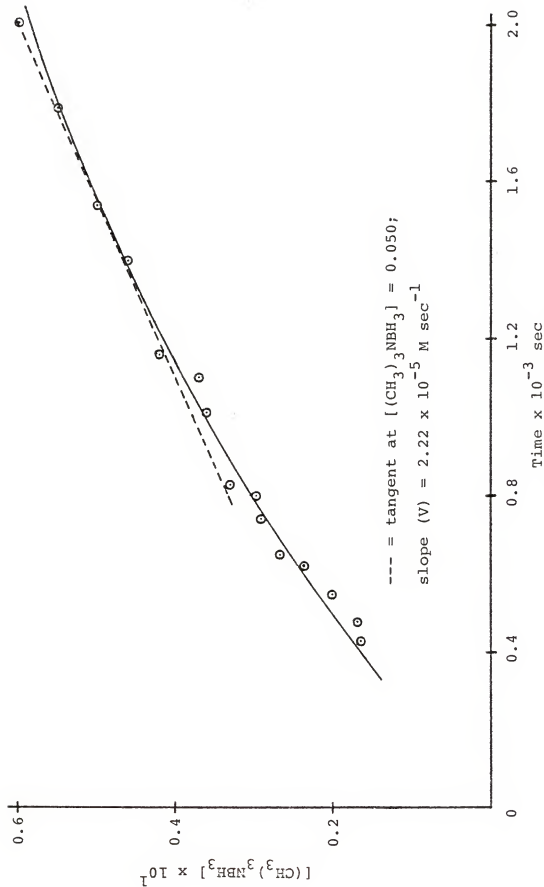


Figure 7. Trimethylamine-borane concentration vs. time plot (-) for  $[\text{pyBH}_3]_0 = 0.500$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.130$ .

Table 3  
Concentrations and Slopes of Tangents for Figures 1 - 7

Figure	Slope (V), <sup>a</sup> M sec <sup>-1</sup> x 10 <sup>-5</sup>	5 + log V	[pyBH <sub>3</sub> ] <sup>b</sup>	2 + log [pyBH <sub>3</sub> ]	[(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I] <sup>c</sup>	2 + log [(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I]
1	13.7	1.137	0.450	1.653	0.450	1.653
2	11.3	1.053	0.350	1.544	0.450	1.653
3	5.20	0.716	0.170	1.230	0.450	1.653
4	2.23	0.348	0.075	0.875	0.450	0.653
5	8.95	0.952	0.450	1.653	0.320	1.505
6	5.70	0.756	0.450	1.653	0.200	1.301
7	2.22	0.346	0.450	1.653	0.080	0.903

<sup>a</sup> V is the slope of the tangent to the [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>] vs. time plot at [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>] = 0.050

<sup>b</sup> [pyBH<sub>3</sub>] is the concentration of pyridine-borane when [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>] = 0.050; i.e., [pyBH<sub>3</sub>]<sub>0</sub> = [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>]<sub>0</sub> = 0.050 M

<sup>c</sup> [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I] is the concentration of trimethylamine-iodoborane when [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>] = 0.050; i.e., [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I] = [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>]<sub>0</sub> - [(CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>]<sub>t</sub> = 0.050 M

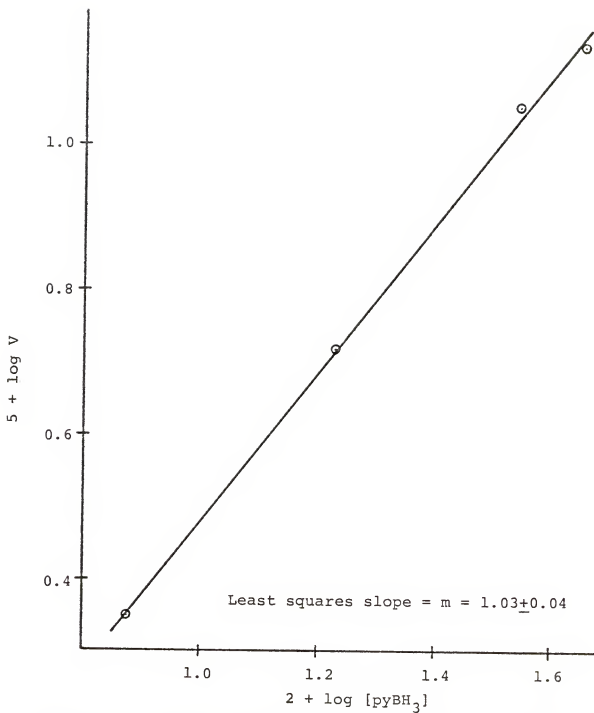


Figure 8. Plot to determine the order ( $m$ ) of the hydrogen-iodine exchange reaction with respect to pyridine-borane.



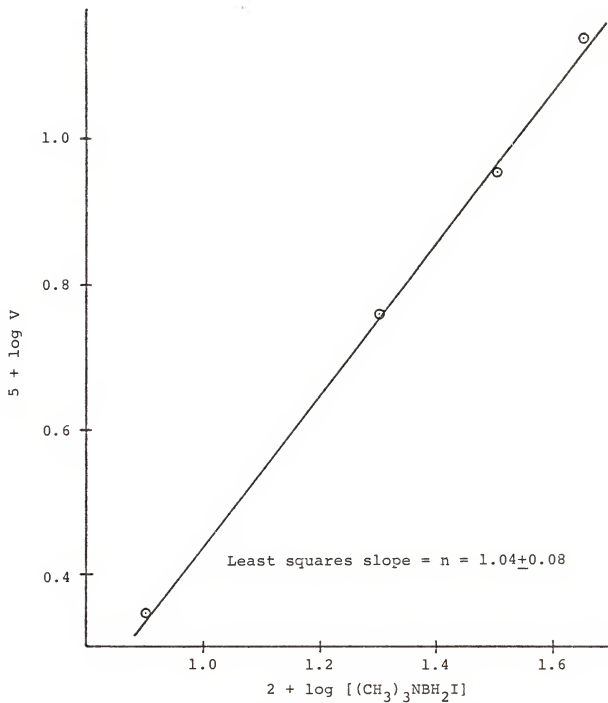


Figure 9. Plot to determine the order ( $n$ ) of the hydrogen-iodine exchange reaction with respect to trimethylamine-iodoborane.

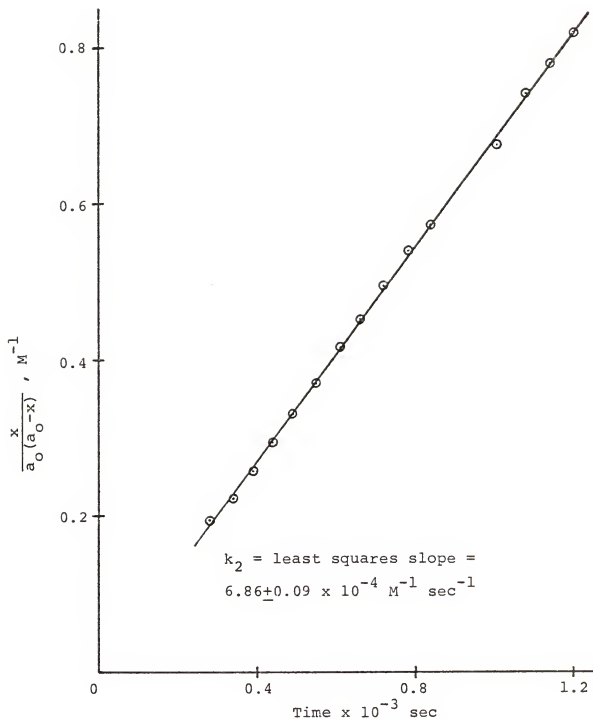


Figure 10. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = [(CH_3)_3NBH_2I]_0 = 0.500$ .

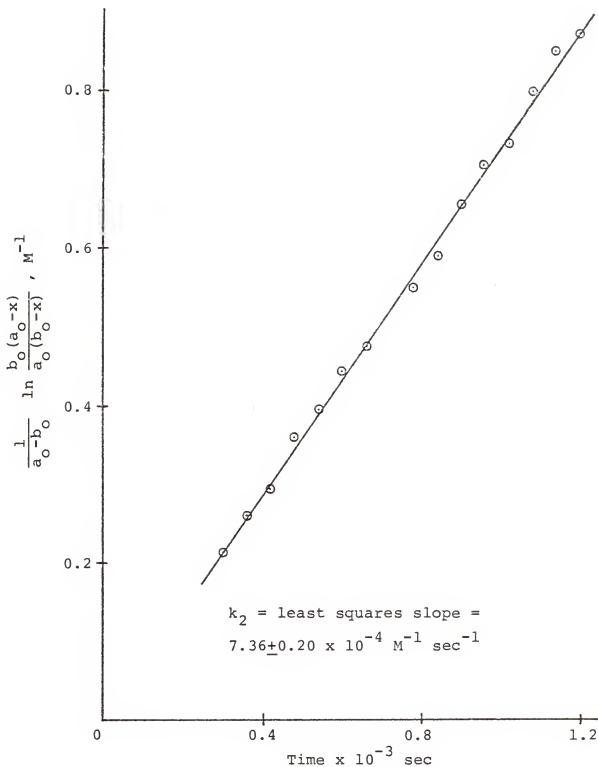


Figure 11. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = 0.400$ , and  $[(CH_3)_3NBH_2I]_0 = 0.500$ .

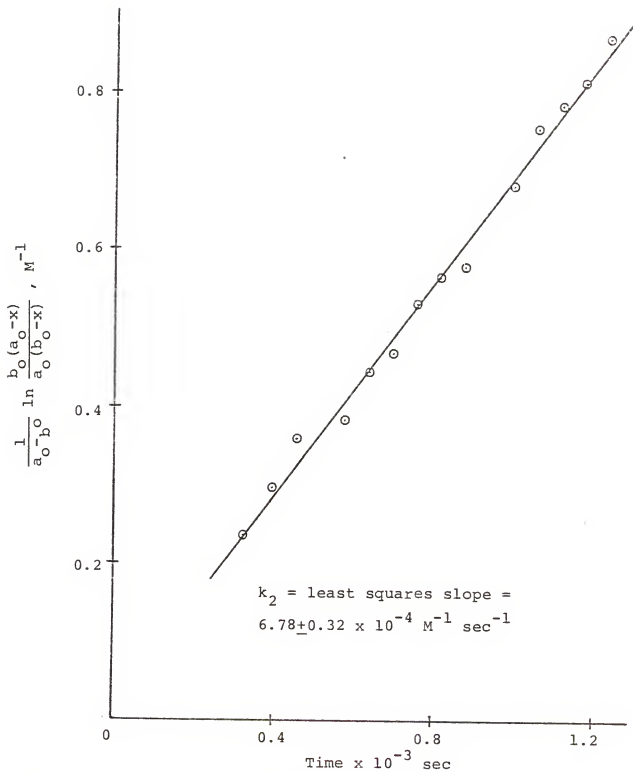


Figure 12. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = 0.220$ , and  $[(CH_3)_3BH_2I]_0 = 0.500$ .

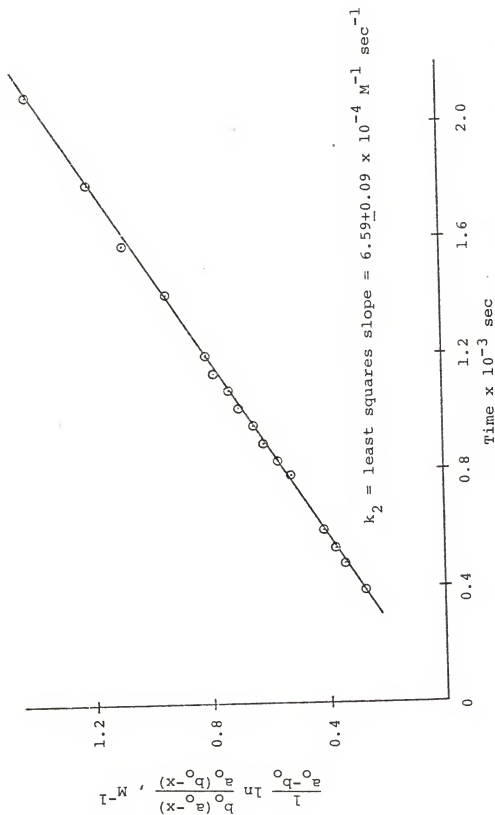


Figure 13. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[\text{pyBH}_3]_0 = 0.125$ , and  $[(\text{CH}_3)_3\text{NBH}_2]_0 = 0.500$ .

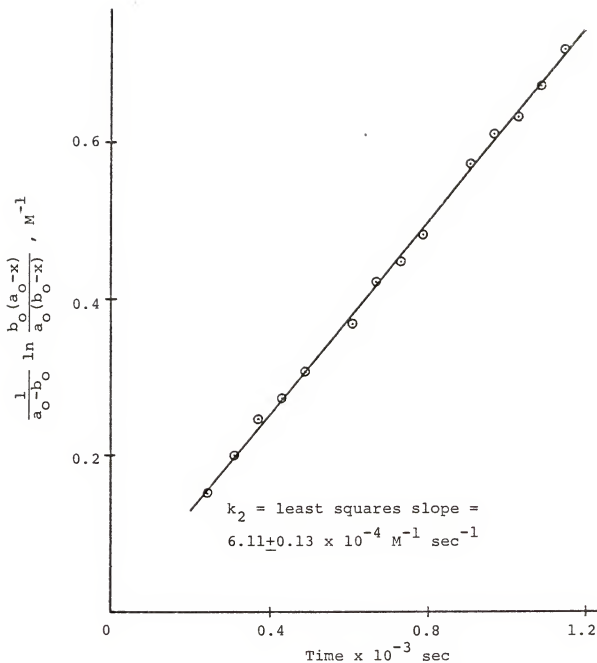


Figure 14. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = 0.500$ , and  $[(CH_3)_3NBH_2I]_0 = 0.370$ .

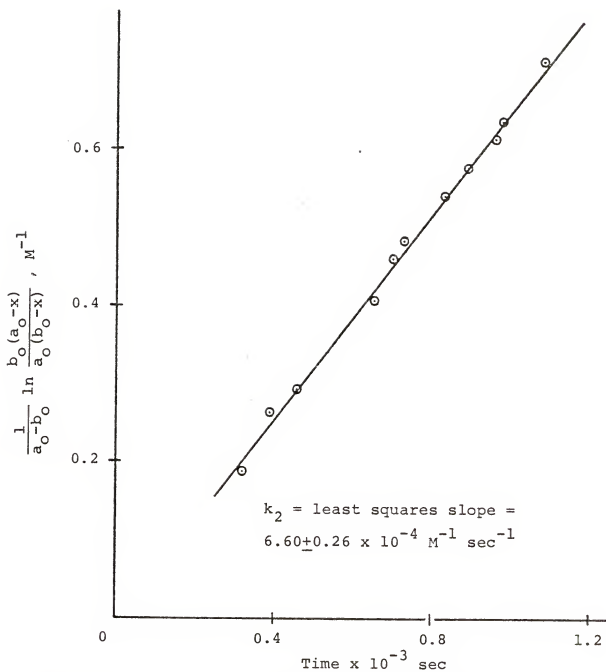


Figure 15. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[\text{pyBH}_3]_0 = 0.500$ , and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.250$ .

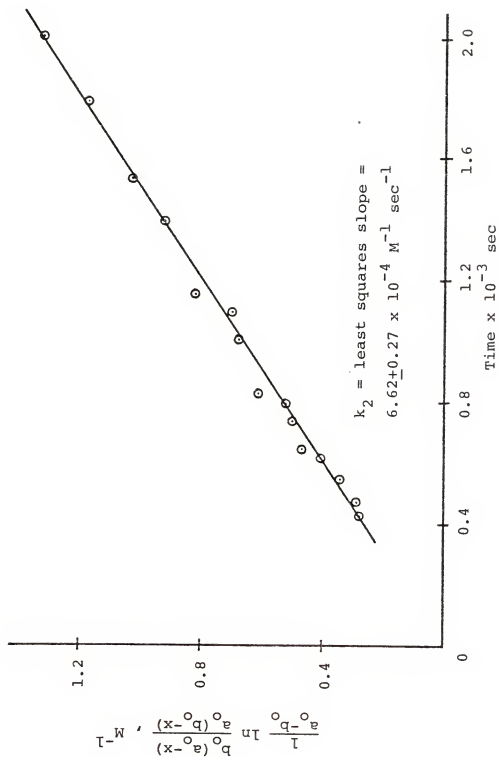


Figure 16. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[\text{pyBH}_3]_0 = 0.500$ , and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.130$ .



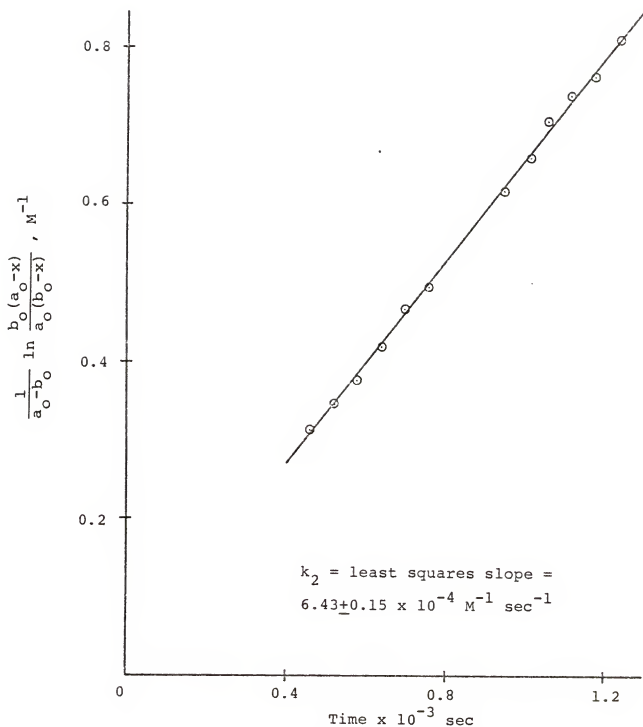


Figure 17. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = 0.500$ ,  $[(CH_3)_3NBH_2I]_0 = 0.250$ , and  $[(n-C_4H_9)_4N^+I^-]_0 = 0.250$ .

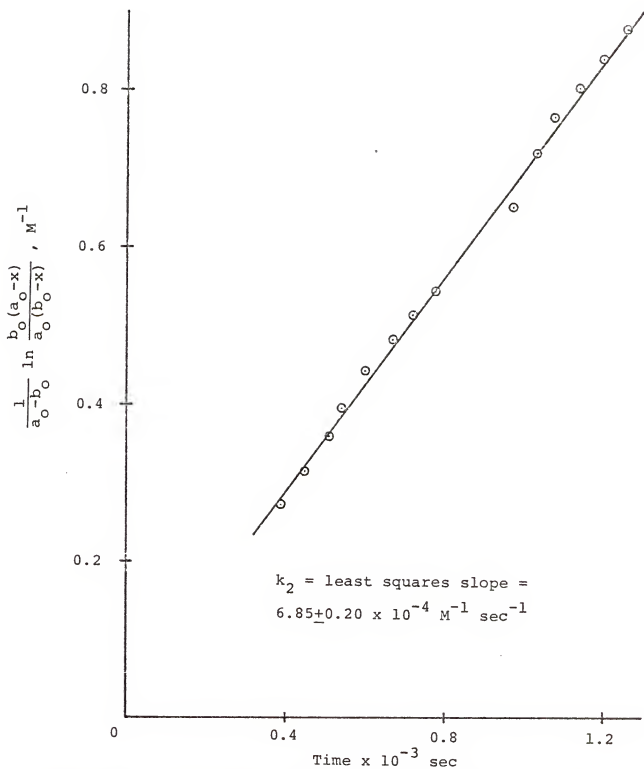


Figure 13. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[\text{pyBH}_3]_0 = 0.500$ ,  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.250$ , and  $[(\text{n-C}_4\text{H}_9)_4\text{N}^+\text{I}^-]_0 = 0.130$ .

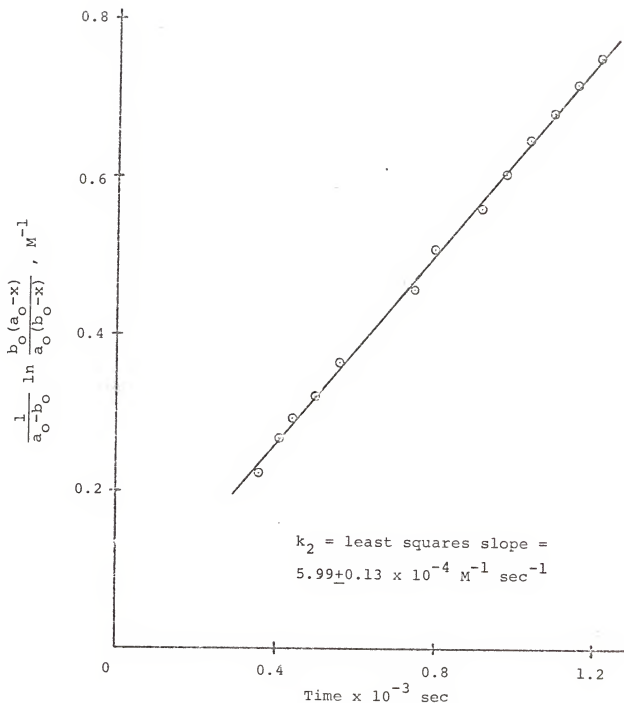


Figure 19. Second order plot for the hydrogen-iodine exchange reaction of pyridine-borane with trimethylamine-iodoborane;  $[pyBH_3]_0 = 0.500$ ,  $[(CH_3)_3NBH_2I]_0 = 0.250$ , and  $[(n-C_4H_9)_4N^+I^-]_0 = 0.050$ .

Table 4  
Second Order Rate Data for the Hydrogen-Iodine  
Exchange Reaction of Pyridine-Borane with Trimethylamine-Iodoborane at 35°C

$[\text{pyBH}_3]_0$	$[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0$	Figure	$k_2, \text{M}^{-1} \text{sec}^{-1} \times 10^4$ (least squares slope)	Intercept ( $t=0$ ) $\text{M}^{-1}$
0.500	0.500	10	$6.86 \pm .09$	$-0.005 \pm .003$
0.400	0.500	11	$7.36 \pm .20$	$-0.007 \pm .006$
0.220	0.500	12	$6.78 \pm .32$	$0.014 \pm .009$
0.125	0.500	13	$6.59 \pm .09$	$0.019 \pm .004$
0.500	0.370	14	$6.11 \pm .13$	$0.007 \pm .004$
0.500	0.250	15	$6.60 \pm .26$	$-0.010 \pm .006$
0.500	0.130	16	$6.62 \pm .27$	$0.003 \pm .013$
$0.500^a$	0.250	17	$6.43 \pm .15$	$0.011 \pm .004$
$0.500^b$	0.250	18	$6.85 \pm .20$	$0.015 \pm .006$
$0.500^c$	0.250	19	$5.99 \pm .13$	$0.019 \pm .004$

<sup>a</sup>  $[\text{H-C}_4\text{H}_9)_4\text{N}^+\text{I}^-] = 0.250$

<sup>b</sup>  $[\text{H-C}_4\text{H}_9)_4\text{N}^+\text{I}^-] = 0.130$

<sup>c</sup>  $[\text{H-C}_4\text{H}_9)_4\text{N}^+\text{I}^-] = 0.050$

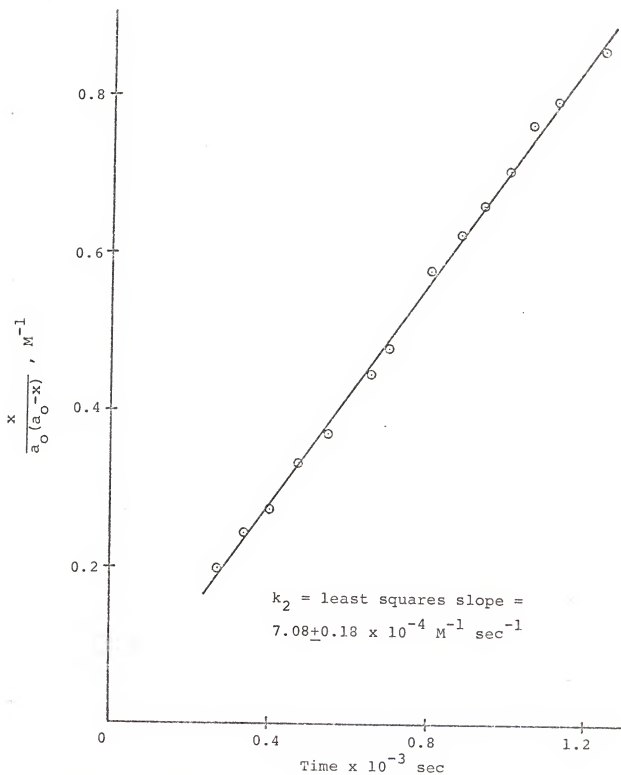


Figure 20. Second order plot for the hydrogen-iodine exchange reaction of 4-methylpyridine-borane with trimethylamine-iodoborane;  $[4\text{-CH}_3\text{FyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

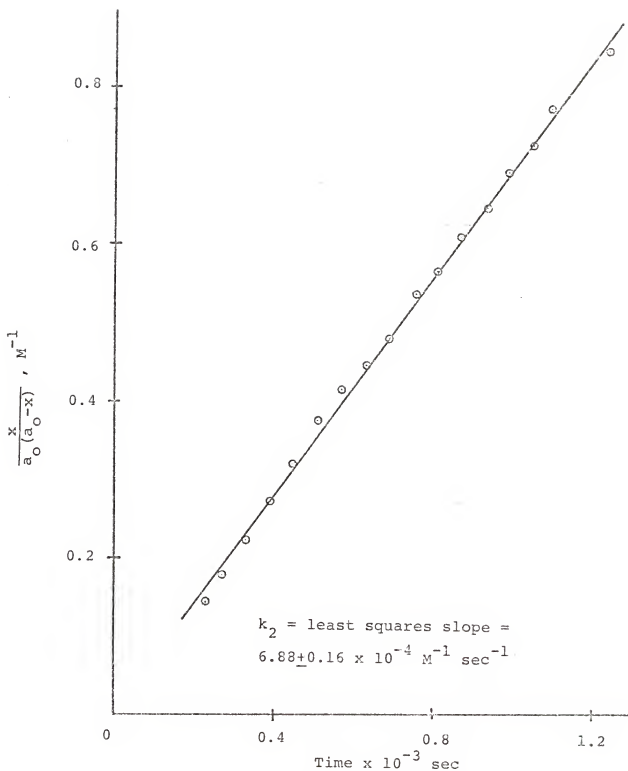


Figure 21. Second order plot for the hydrogen-iodine exchange reaction of 4-methylpyridine-borane with trimethylamine-iodoborane;  $[4\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

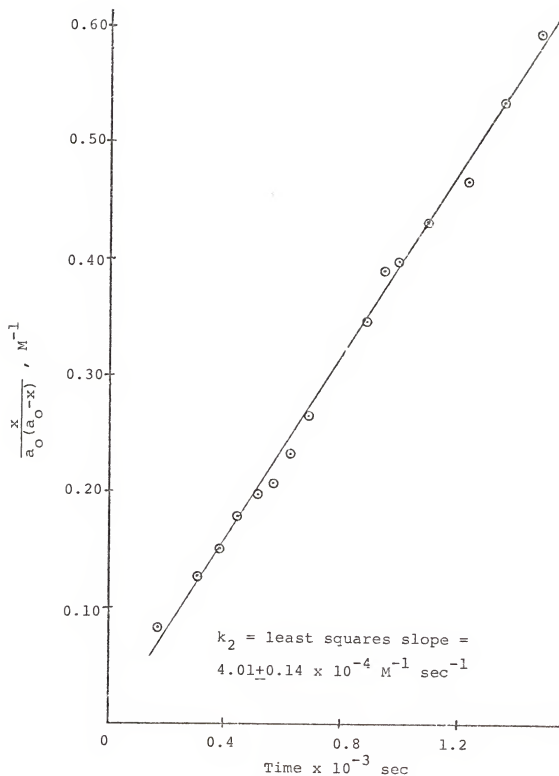


Figure 22. Second order plot for the hydrogen-iodine exchange reaction of 4-chloropyridine-borane with trimethylamine-iodoborane;  $[4\text{-ClpyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

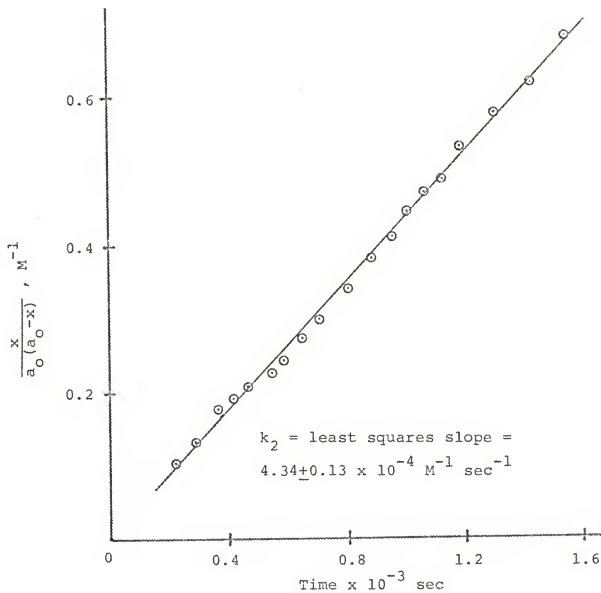


Figure 23. Second order plot for the hydrogen-iodine exchange reaction of 4-chloropyridine-borane with trimethylamine-iodoborane;  $[4\text{-ClpyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .



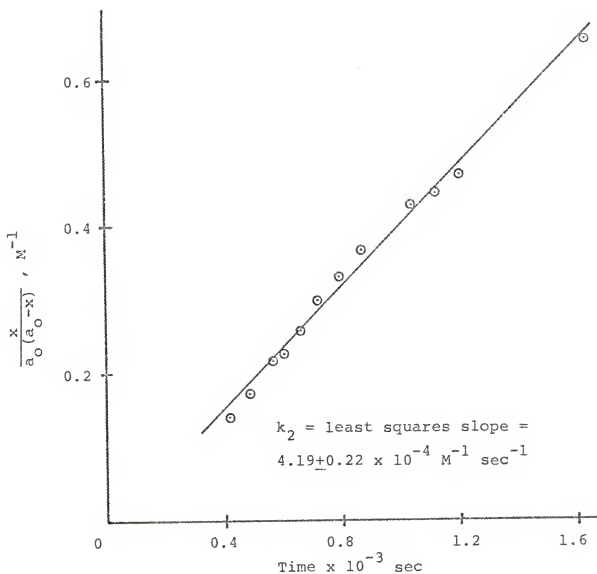


Figure 24. Second order plot for the hydrogen-iodine exchange reaction of 2-methylpyridine-borane with trimethylamine-iodoborane;  $[2\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

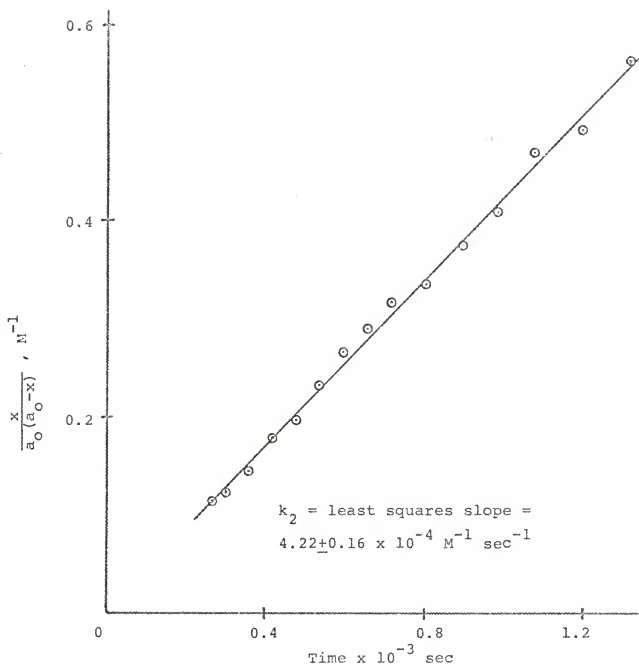


Figure 25. Second order plot for the hydrogen-iodine exchange reaction of 2-methylpyridine-borane with trimethylamine-iodoborane;  $[2\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

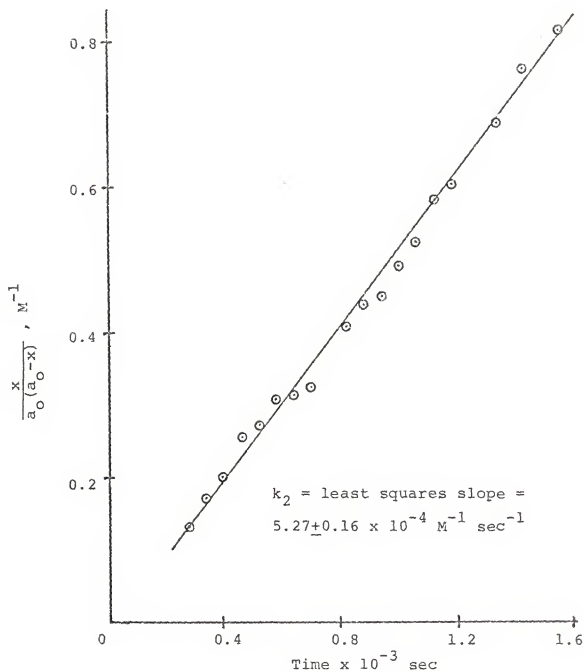


Figure 26. Second order plot for the hydrogen-iodine exchange reaction of 2,6-dimethylpyridine-borane with trimethylamine-iodoborane;  $[2,6-(CH_3)_2PyBH_3]_0 = [(CH_3)_3NBH_2I]_0 = 0.500$ .

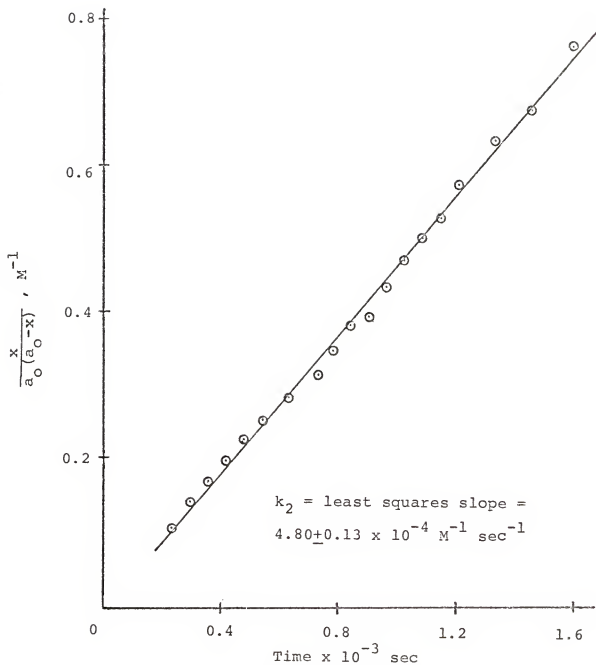


Figure 27. Second order plot for the hydrogen-iodine exchange reaction of 2,6-methylpyridine-borane with trimethylamine-iodoborane;  $[2,6-(\text{CH}_3)_2\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

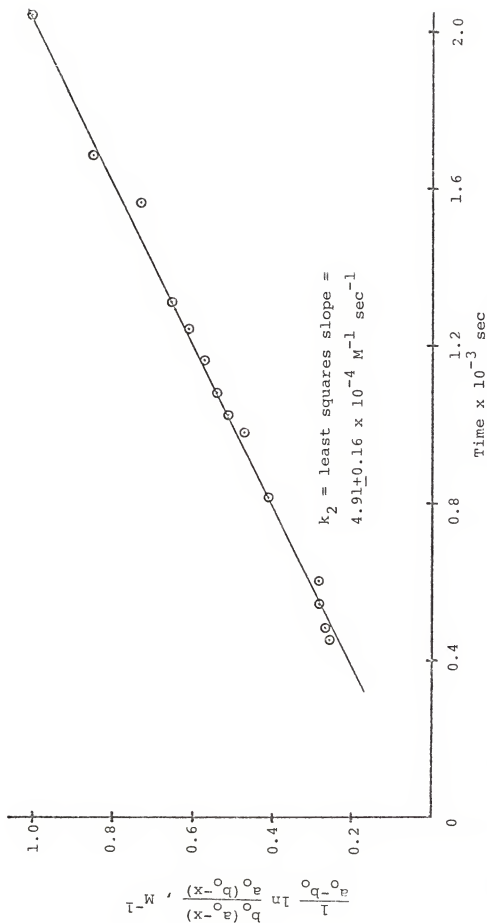


Figure 28. Second order plot for the hydrogen-iodine exchange reaction of 2-t-butylpyridine-borane with trimethylamine-iodoborane;  $[2-C(CH_3)_3pyBH_3]_0 = 0.390$  and  $[(CH_3)_3NBH_2I]_0 = 0.500$ .

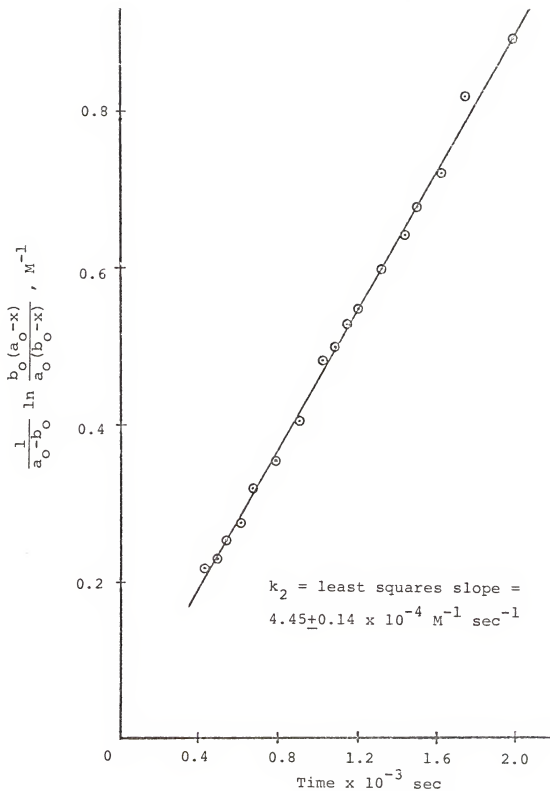


Figure 29. Second order plot for the hydrogen-iodine exchange reaction of 2-*t*-butylpyridine-borane with trimethylamine-iodoborane;  $[2\text{-}\bar{\text{C}}(\text{CH}_3)_3\text{PyBH}_3]_0 = 0.376$  and  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

Table 5  
Second Order Rate Data for the Hydrogen-Iodine Exchange Reactions  
of Substituted Pyridine-Boranes with Trimethylamine-Iodoborane

R in R-py	Temp. °C	Figure	[R-pyBH <sub>3</sub> ] <sub>0</sub>	[(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I] <sub>0</sub>	k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>4</sup> (least squares slope)	Intercept (t=0), M <sup>-1</sup>
4-CH <sub>3</sub>	35	20	0.500	0.500	7.08 ± 0.18	-0.005+0.005
4-CH <sub>3</sub>	35	21	0.500	0.500	6.88 ± 0.16	0.004+0.005
4-CH <sub>3</sub> <sup>a</sup>	35	30	0.250	0.500	6.69 ± 0.19	0.018+0.009
4-CH <sub>3</sub>	0	31	0.500	0.500	0.401 ± 0.037	-0.004+0.018
4-CH <sub>3</sub> <sup>b</sup>	0	32	0.500	0.500	0.397 ± 0.054	0.014+0.024
4-Cl	35	22	0.500	0.500	4.01 ± 0.14	-0.001+0.005
4-Cl	35	23	0.500	0.500	4.34 ± 0.13	0.000+0.005
2-CH <sub>3</sub>	35	24	0.500	0.500	4.19 ± 0.22	-0.018+0.007
2-CH <sub>3</sub>	35	25	0.500	0.500	4.22 ± 0.16	0.001+0.005
2,6-(CH <sub>3</sub> ) <sub>2</sub>	35	26	0.500	0.500	5.27 ± 0.16	0.001+0.005
2,6-(CH <sub>3</sub> ) <sub>2</sub>	35	27	0.500	0.500	4.80 ± 0.13	-0.009+0.005
2-(CH <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	35	28	0.390	0.500	4.91 ± 0.16	0.013+0.007
2-(CH <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	35	29	0.376	0.500	4.45 ± 0.14	0.014+0.006

<sup>a</sup> The boron-hydrogens were substituted with deuterium

<sup>b</sup> The nmr tube also contained a pressure of diborane

Table 6  
Average Second Order Rate Constants for the Hydrogen-Iodine  
Exchange Reactions of Trimethylamine-Iodoborane  
with Pyridine-Boranes at 35°C

R in R-py	$k_2, \text{M}^{-1} \text{sec}^{-1} \times 10^4$	Keq	$k_{-2}, \text{M}^{-1} \text{sec}^{-1} \times 10^4^a$
H	6.69	2.18	3.07
4-CH <sub>3</sub>	6.98	3.96	1.76
4-Cl	4.18	1.29	3.24
2-CH <sub>3</sub>	4.21	1.78	2.37
2,6-(CH <sub>3</sub> ) <sub>2</sub>	5.04	3.56	1.41
2-C(CH <sub>3</sub> ) <sub>3</sub>	4.68	1.89	2.50

<sup>a</sup> Calculated from  $k_{-2} = k_2/\text{Keq}$



dine derivatives.

The reaction mixtures were prepared by syringing measured quantities of stock solutions of the pyridine-borane (1.000 M) and trimethylamine-iodoborane (1.000 M) into nmr tubes. In those runs containing tetra-n-butylammonium iodide, appropriate volumes of a 1.000 M stock solution of the salt were syringed into the nmr tube before the addition of the other reagents. When additional dilution was required, the appropriate volume of methylene chloride was also syringed into the nmr tube before adding the last reagent. The stock solutions were prewarmed to the reaction temperature (35°C) before withdrawal of the aliquots. The contents of the nmr tubes were held at 35°C before the addition of the last reagent. Since the densities of the stock solutions were observed to be significantly sensitive to temperature, they were brought to volume at the reaction temperature of 35°C. The nmr tubes were shaken immediately after the addition of the final reagent with the initial time marked at this moment. The nmr tubes were promptly placed into the thermostatted sample probe of the instrument (35°C), and the first spectra were taken as soon as possible.

The procedure was slightly different for 2-t-butylpyridine-borane, in which case a known volume of stock trimethylamine-iodoborane solution was added to a weighed sample of the amine-borane in a volumetric flask and the solution

brought to volume at 35°C before transferal to an nmr tube. The initial concentration of 2-t-butylpyridine-borane was determined by integration of the 2-t-butyl region of the  $^1\text{H}$  nmr spectrum (85 Hz to 110 Hz) vs. the trimethylamine area (140 Hz to 180 Hz).

Similarly, the initial rate of deuterium-iodine exchange for the reaction of 4-methylpyridine-borane- $\text{d}_3$  with trimethylamine-iodoborane- $\text{d}_2$  was determined at 35°C in methylene chloride. For this system, it was unnecessary to correct the trimethylamine-borane integral area for boron-hydrogen content. The least squares plot of the integrated second order rate expression vs. time for this reaction is given in Figure 30.

In addition, the initial rate of hydrogen-iodine exchange between 4-methylpyridine-borane and trimethylamine-iodoborane in methylene chloride was determined at 0°C. Stock solutions (1.000 M) of each solute were cooled to -10°C with a Mini-Freezer in the Dri-Lab before withdrawal of the aliquots which were mixed in an nmr tube. The sample was immediately removed from the Dri-Lab and cooled to -196°C. Then the sample was warmed to 0°C in an ice bath before introduction into the precooled nmr probe (0°C) at the start of the kinetic run.

In a similar manner, the initial rate of exchange for a sample of 4-methylpyridine-borane and trimethylamine-iodoborane under a pressure of diborane was determined at 0°C. An nmr tube fitted with a ground glass joint was loaded with

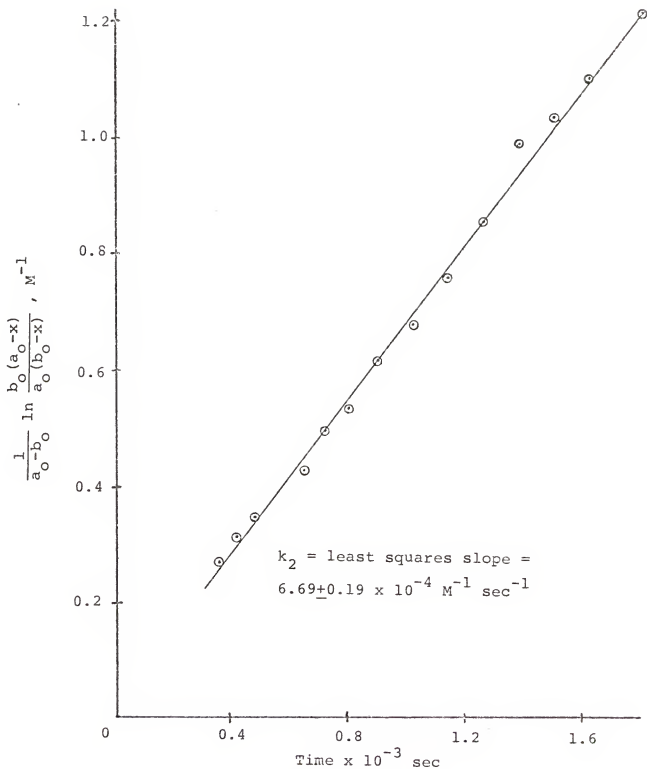
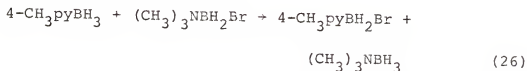


Figure 30. Second order plot for the deuterium-iodine exchange reaction of 4-methylpyridine-borane- $d_3$  with trimethylamine-iodoborane- $d_2$ ;  $[4\text{-CH}_3\text{PyBD}_3]_0 = [(\text{CH}_3)_3\text{NBD}_2\text{I}]_0 = 0.500$ .

0.40 ml each of precooled ( $-10^{\circ}\text{C}$ ) 1.000 M 4-methylpyridine-borane and 1.000 M trimethylamine-iodoborane. The sample was immediately removed from the Dri-Lab, cooled to  $-196^{\circ}\text{C}$ , and evacuated on the vacuum line. Then freshly purified diborane ( $5.0 \times 10^{-5}$  moles) was condensed onto the sample, and the tube was sealed. From an estimate of the volume of the sealed tube, the pressure of diborane in it was approximated to be 0.95 atm if none of the gas dissolved. The quantity of diborane added corresponded to 50% of the amount that could be formed by complete reaction of the equilibrium concentrations of 4-methylpyridine-borane and 4-methylpyridine-iodoborane according to equation 43. The sample was warmed to  $0^{\circ}\text{C}$  in an ice bath before insertion into the nmr probe ( $0^{\circ}\text{C}$ ) at the start of the kinetic run. The results of the  $0^{\circ}\text{C}$  runs are given in Figures 31 and 32 and in Table 5.

#### Hydrogen-bromine and hydrogen-chlorine exchange

The approximate initial rate of hydrogen-bromine exchange between 4-methylpyridine-borane and trimethylamine-bromoborane was similarly determined in methylene chloride at room temperature ( $24 \pm 2^{\circ}\text{C}$ ).



The reaction was monitored in the nmr spectrum by integration of the resonances in the 430 to 470 Hz region corresponding to the 3,5-aromatic protons of 4-methylpyridine-borane and 4-methylpyridine-bromoborane. Likewise, an esti-

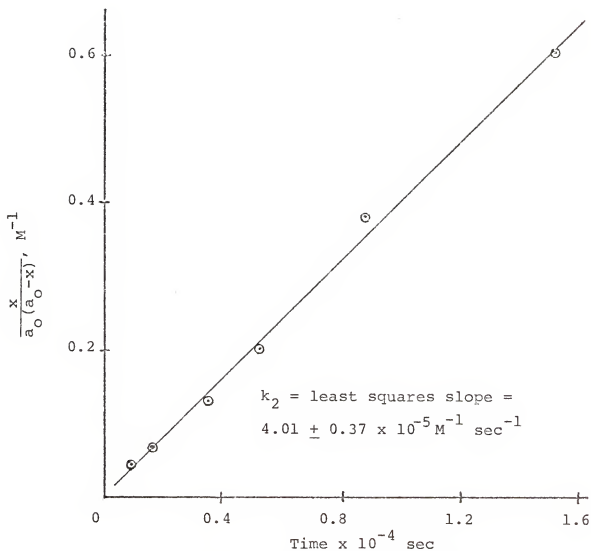


Figure 31. Second order plot for the hydrogen iodine exchange reaction of 4-methylpyridine-borane with trimethylamine-iodoborane at  $0^\circ\text{C}$ ;  $[4\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{BH}_2\text{I}]_0 = 0.500$ .

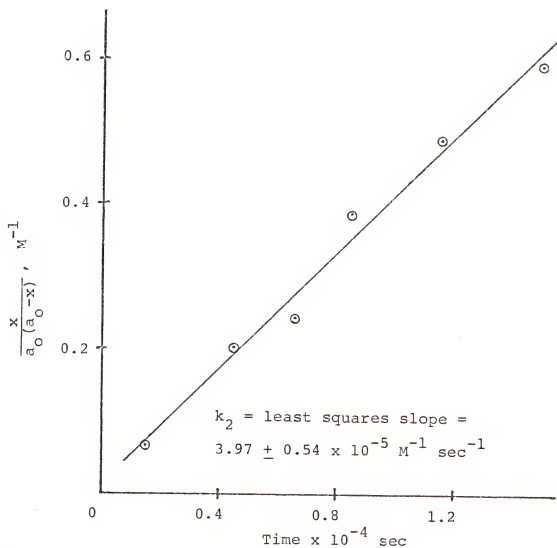
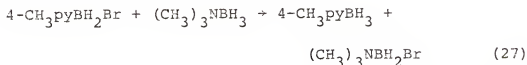


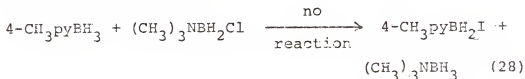
Figure 32. Second order plot for the hydrogen-iodine exchange reaction of 4-methylpyridine-borane with trimethylamine-iodoborane under a pressure of diborane at 0°C;  $[4\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.500$ .

mate of the initial rate of the reverse reaction (equation 27) was made by integration of the aliphatic region of the nmr spectrum. The reaction was run in methylene chloride solution at room temperature ( $24 \pm 2^\circ\text{C}$ ).



The trimethylamine-bromoborane area was estimated by direct integration of its signal, whereas the trimethylamine-borane area was estimated by subtraction of the 4-methylpyridine contribution from the aliphatic integral area. The effect on  $k_2$  of the substitution of bromine for iodine on boron can be seen in Table 7. The rate constants and error limits in Table 7 for hydrogen-bromine exchange include allowances for a side reaction analogous to equation 43.

A solution containing 4-methylpyridine-borane (1.0 M) and trimethylamine-chloroborane (1.0 M) failed to produce any detectable hydrogen-chlorine exchange after 20 days at room temperature ( $24 \pm 2^\circ\text{C}$ ).



Likewise, a solution of 1.0 M 4-methylpyridine-chloroborane and 1.0 M trimethylamine-borane failed to undergo any detectable exchange after 20 days at room temperature.

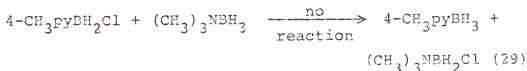


Table 7  
Approximate Second Order Rate Constants for the  
Hydrogen-Halogen Exchange Reactions of  
4-Methylpyridine-Borane with Trimethylamine-Haloboranes  
at 24 ± 2°C

x	$k_2, \text{M}^{-1} \text{sec}^{-1}$
I <sup>a</sup>	$6.0 \pm 0.3 \times 10^{-4}$
Br	$9 \pm 3 \times 10^{-7}$
Cl <sup>b</sup>	No reaction in 20 days

<sup>a</sup> Estimated from an Arrhenius treatment of  $k_2$  at 35°C and 0°C

<sup>b</sup> Initial concentrations of each reagent were approximately 1.0 M



At these concentrations, approximately 1% reaction according to equations 28 or 29 would be detectable in the 430 to 460 Hz region of the  $^1\text{H}$  nmr spectrum, corresponding to the 3,5-ring protons of the expected products.

Kinetics of the Reactions of Pyridine-Boranes with Pyridine-Iodoboranes to Produce Diborane and Bis(pyridine)boronium Iodides

Preparation of equimolar mixtures of pyridine-boranes and pyridine-iodoboranes

Unless otherwise indicated, equimolar mixtures of a pyridine-borane ( $\text{R-pyBH}_3$ ) and its monoiodinated derivative ( $\text{R-pyBH}_2\text{I}$ ) were prepared by the following methods. Dry solvent was added to a weighed quantity of the pyridine-borane in a volumetric flask in the Dri-Lab, and solid iodine was added a piece at a time to the stirred solution. The quantity of iodine used was the amount required to monoiodinate half of the substituted pyridine-borane.<sup>44,45</sup> Other solutes (if any) were added, and the solution was brought to volume with solvent. Freshly prepared solutions were used for each experiment.

Rate parameters for 4-methylpyridine-borane

Two general procedures were employed to follow the progress of reaction 43 for the 4-methylpyridine derivative in order to determine the rate parameters. The first of these (Method A) was to integrate the change in the  $^1\text{H}$  nmr signal of the reaction mixture. The combined integral area of the reactants was monitored relative to the area of the bis(pyridine)boronium iodide produced, or relative to the area of

a quantitative internal standard. The second procedure (Method B) used to follow the course of the reaction, was to quantitatively collect the insoluble iodide salt of the boron cation.

Overall order with respect to the starting materials.

Both methods were employed to determine the overall order of the reaction with respect to the starting materials. Method A was used at 60.0°C with benzene as a solvent, and with 1,3,5-trimethylbenzene (mesitylene; bp 160-163°C, dried over  $\text{CaH}_2$ ) as a quantitative internal standard for  $^1\text{H}$  nmr integrations. A 20.0 ml portion of a solution of 0.500 M 4-methylpyridine-borane, 0.500 M 4-methylpyridine-iodoborane, and 0.0984 M mesitylene was placed in a 100 ml 3-neck flask fitted with a reflux condenser and a serum cap through which liquid samples could be drawn periodically via syringe for  $^1\text{H}$  nmr analysis. The aliphatic region of the  $^1\text{H}$  nmr spectrum of the initial reaction mixture before any heating exhibited a sharp singlet at 130 Hz representing the mesitylene methyl groups, and a broad singlet at 105 Hz attributed to the combined methyl signals of 4-methylpyridine-borane and 4-methylpyridine-iodoborane. In addition, another singlet at 118 Hz was detected with an integrated area of 6.9% of the total 4-methylpyridine aliphatic resonances.

The reaction flask was placed in a 60.0°C constant temperature bath at time zero, and liquid samples were drawn periodically over a length of several hours. Each sample was syringed into a nmr tube, quenched to room temperature,

and the  $^1\text{H}$  nmr spectrum was taken immediately. The concentrations of the starting materials at each time were determined by integration of the reactant methyl resonances vs. the mesitylene aliphatic signal. Table 3 lists the calculated first, second, and third order rate constants for the reaction, including relative standard deviations (Sr). The results of the integral graphical method are presented in first, second, and third order plots in Figures 33 - 36.

The reaction was also investigated using Method A in methylene chloride at 25°C with initial concentrations of 0.50 M for each reactant. The reaction was monitored by integration of the 3,5-pyridine proton resonances of the boronium iodide produced vs. those of the starting materials. Poor resolution of the reactant and product resonances limited the accuracy of the measurements. The results of the second order calculations by the tabular method and the integral graphical method are presented in Table 9 and Figure 37, respectively.

The overall order of the reaction and the rate constant at 70.0°C were also determined in benzene by Method B. Samples of a stock solution of 0.100 M 4-methylpyridine-borane and 0.100 M 4-methylpyridine-iodoborane were pipetted into reaction tubes each fitted with a serum cap and a syringe needle to allow the exit of gases. The reaction tubes were removed from the Dri-Lab one at a time, and immersed in a 100°C bath for a predetermined period necessary to bring the temperature of the reaction mixture to approximately 70°C.

Table 8  
Rate Constants for Bis(4-methylpyridine)boronium Iodide  
Formation in Benzene at 60.0°C

Sample	Time, sec. x 10 <sup>-4</sup>	[4-CH <sub>3</sub> pyBH <sub>3</sub> ] sec <sup>-1</sup> x 10 <sup>5</sup>	k <sub>1</sub> , sec <sup>-1</sup> x 10 <sup>5</sup>	k <sub>2</sub> <sup>a</sup> , M <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>5</sup>	k <sub>2</sub> <sup>b</sup> , M <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>5</sup>	k <sub>3</sub> , M <sup>-2</sup> sec <sup>-1</sup> x 10 <sup>4</sup>
1	0.180	0.433	7.80	17.2	8.84	3.78
2	0.360	0.415	5.06	11.4	7.48	2.59
3	0.580	0.380	4.78	10.9	8.27	2.36
4	0.750	0.366	4.08	9.78	7.73	2.08
5	1.22	0.313	3.85	9.76	8.53	2.54
6	1.98	0.271	3.08	8.50	7.78	2.39
7	4.23	0.181	2.39	8.30	7.95	3.13
8	6.82	0.126	2.02	8.71	8.51	4.30
Mean	----	-----	4.14	10.6	8.14	2.90
Sr (%)	----	-----	44.2	27.4	5.84	26.8

<sup>a</sup> [4-CH<sub>3</sub>pyBH<sub>3</sub>]<sub>0</sub> = [4-CH<sub>3</sub>pyBH<sub>2</sub>I]<sub>0</sub> = 0.500

<sup>b</sup> [4-CH<sub>3</sub>pyBH<sub>3</sub>]<sub>0</sub> = [4-CH<sub>3</sub>pyBH<sub>2</sub>I]<sub>0</sub> = 0.465

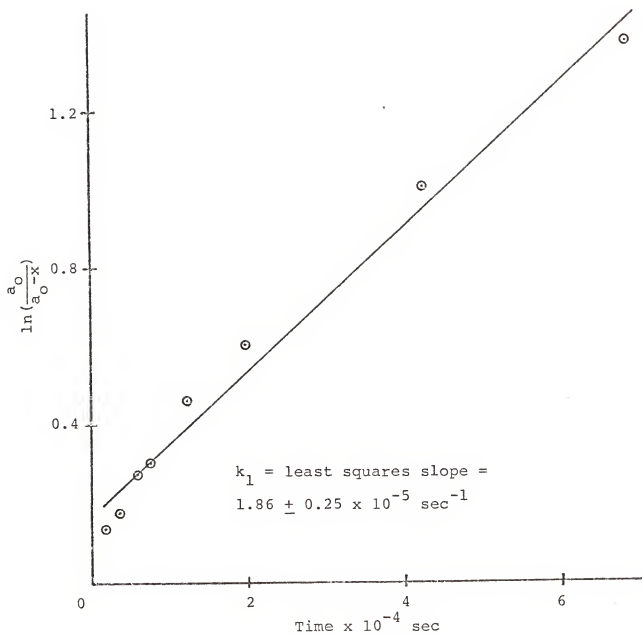


Figure 33. First order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 60.0°C.

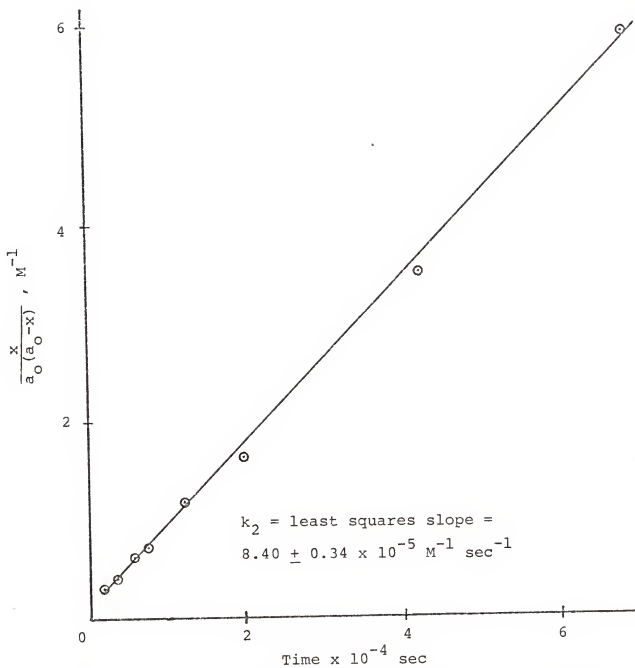


Figure 34. Second order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 60.0°C

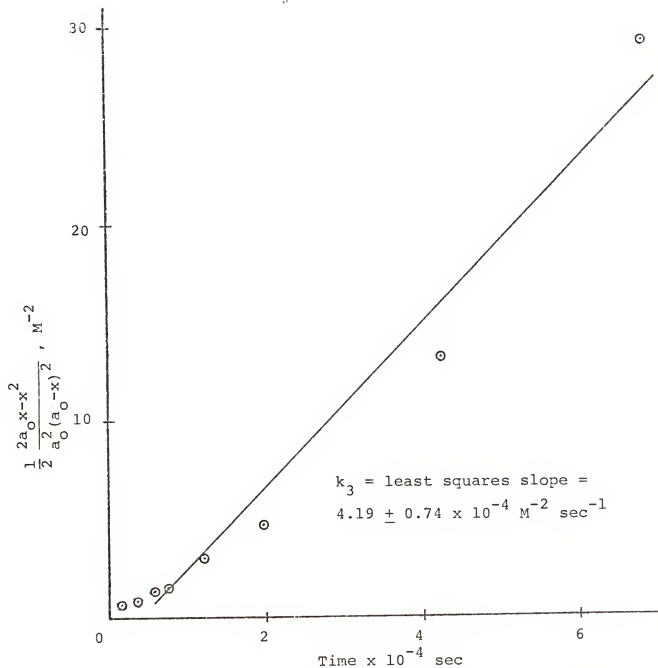


Figure 35. Third order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 60.0°C.

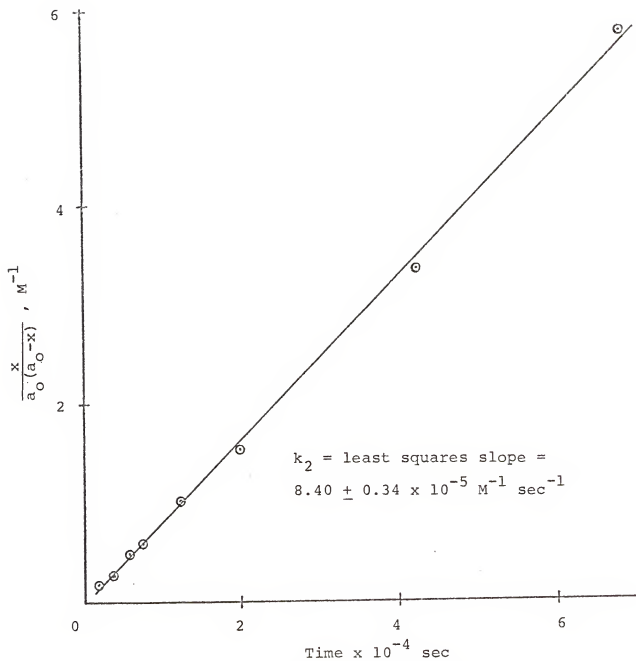


Figure 36. Modified second order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 60.0°C.



Table 9  
Second Order Rate Constants for  
Bis(4-methylpyridine)boronium Iodide  
Formation in Methylene Chloride at 25°C

Time, sec x 10 <sup>-4</sup>	[4-CH <sub>3</sub> pyBH <sub>3</sub> ] <sup>a</sup>	k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>5</sup>
0.54	0.46	3.5
1.53	0.44	1.8
7.29	0.40	0.64
15.9	0.36	0.47

<sup>a</sup> [4-CH<sub>3</sub>pyBH<sub>3</sub>]<sub>0</sub> = [4-CH<sub>3</sub>pyBH<sub>2</sub>I]<sub>0</sub> = 0.50

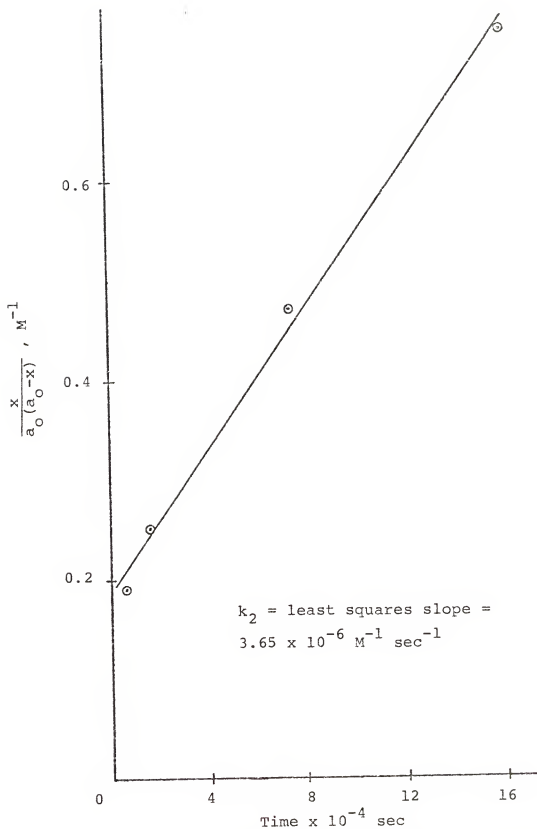


Figure 37. Second order plot for the formation of bis(4-methylpyridine)boronium iodide in methylene chloride at 25°C.

Each reaction tube was then inserted in a 70.0°C constant temperature bath at time zero for that tube. After heating at 70.0°C for the appropriate reaction time, each tube was removed from the constant temperature bath and cooled to approximately 20°C in an ice bath with a flow of dry nitrogen passing through the tube during the cooling process. The tube was then taken into the Dri-Lab, and the white needles which had precipitated were collected by suction filtration on a tared coarse-fritted funnel. The funnel and precipitate were washed thoroughly with 20 ml of benzene, dried under vacuum, and weighed again to obtain the weight of precipitate collected. For each sample the precipitate collected was completely soluble in methylene chloride, so that no hydrolysis products such as boric acid were believed to be present.\*

The reproducibility of Method B and the purity of the bis(4-methylpyridine)boronium iodide product were investigated in a triplicate run with initial 0.125 M concentrations for each reactant, and a reaction time of 100.0 min at 70.0°C. The results presented in Table 10 indicate a reproducibility of better than 2% for the method. The combined precipitates (m p = 190-192°C, dec.) from the three runs were analyzed for present composition with the following results:

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\*Hydrolysis reactions of amine-boranes and amine-haloboranes form boric acid as one product.<sup>46-48</sup>

Table 10  
 Triplicate Runs for Bis(4-methylpyridine)boronium Iodide  
 Formation by Method B in Benzene at 70.0°C

Run <sup>a</sup>	[4-CH <sub>3</sub> pyBH <sub>3</sub> ] <sub>2</sub> O	[4-CH <sub>3</sub> pyBH <sub>2</sub> I] <sub>2</sub> O	Weight of (4-CH <sub>3</sub> py) <sub>2</sub> BH <sub>2</sub> I <sup>+</sup> I <sup>-</sup>
1	0.125	0.125	0.0991 g
2	0.125	0.125	0.1031 g
3	0.125	0.125	0.1009 g
Mean	-----	-----	0.1010 <sup>b</sup> ± 0.0014 g

<sup>a</sup> All reaction times were 100.0 min

<sup>b</sup> Corresponds to 16.5% reaction

C=44.00%, H=4.87%, N=8.43%, I=38.98%, and B=3.35%;  
theory for  $C_{12}H_{16}N_2IB$ :

C=44.21%, H=4.95%, N=8.59%, I=38.93%, and B=3.32%.  
The  $^1H$  nmr spectrum of the compound in methylene chloride exhibited a singlet at 155 Hz attributed to the methyl resonance, and two doublets ( $J=7$  Hz) at 460 Hz and 512 Hz representing the 3,5- and 2,6-aromatic protons, respectively. The infrared spectrum of the boronium iodide contained the following absorptions ( $cm^{-1}$ ): 3040 (wk,s), 3020 (wk,s), 2470 (med,s), 2450 (med,s), 2385 (v wk), 1627 (st,s), 1550 (v wk), 1501 (med,s), 1445 (med,br), 1425 (sh), 1331 (med,s), 1272 (med,s), 1225 (v wk), 1205 (sh), 1191 (wk,s), 1145 (sh), 1142 (st,s), 1112 (wk,s), 1092 (st,s), 1060 (wk,s), 960 (wk,s), 890 (v wk), 860 (v wk), 833 (med,s), 821 (med,s), 743 (med,s), 683 (wk,s), 669 (wk,s), 544 (med,s), 493 (med,s), 464 (wk,s), and 404 (wk,s).

The results of kinetic runs with initial reactant concentrations of 0.100 M and variable reaction times are presented in Table 11 with second order rate constants calculated by the tabular method. Second order plots for the integral graphical method are presented in Figures 38 and 39.

Order with respect to each starting material. Analysis of the preceding experiments established the reaction as second order overall with respect to the starting materials (see the Discussion section). The order of the reaction with respect to each starting material was determined from runs with unequal initial concentrations of the reactants

Table 11  
Second Order Rate Constants for Bis(4-methylpyridine)boronium Iodide  
Formation in Benzene at 70.0°C

Sample	Time, sec $\times 10^{-4}$	$[4\text{-CH}_3\text{pyBH}_3]$	$k_2^a$ $\text{M}^{-1} \text{sec}^{-1}$ $\times 10^4$	$k_2^b$ $\text{M}^{-1} \text{sec}^{-1}$ $\times 10^4$
1	0.900	0.0819	2.46	1.62
2	2.07	0.0684	2.23	1.87
3	3.06	0.0621	1.99	1.75
4	4.15	0.0558	1.91	1.73
5	10.38	0.0369	1.65	1.58
Mean	-----	-----	2.05	1.71
St (s)	-----	-----	15.1	6.7

$$^a [4\text{-CH}_3\text{pyBH}_3]_0 = [4\text{-CH}_3\text{pyBH}_2\text{I}]_0 = 0.100$$

$$^b [4\text{-CH}_3\text{pyBH}_3]_0 = [4\text{-CH}_3\text{pyBH}_2\text{I}]_0 = 0.093$$

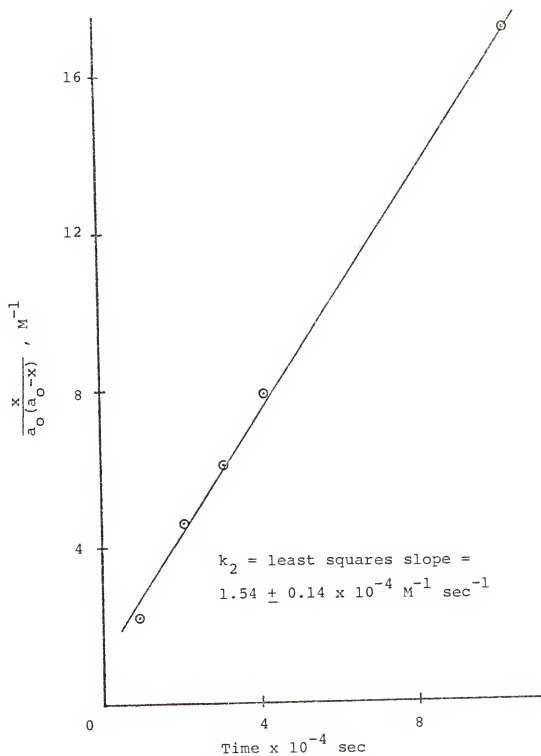


Figure 38. Second order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 70.0°C.

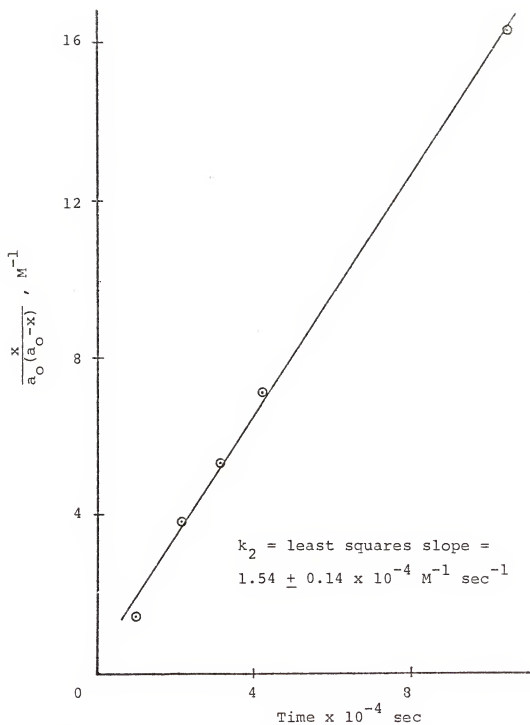


Figure 39. Modified second order plot for the formation of bis(4-methylpyridine)boronium iodide in benzene at 70.0°C.



using Method B at 70.0°C in benzene. The initial concentrations of the reactants were varied by using appropriate aliquots of 1.00 M 4-methylpyridine-borane and 1.00 M 4-methylpyridine-iodoborane stock solutions for a constant reaction time of 100.0 min. Table 12 lists the results of second order calculations for  $q$  and  $r$  equal to one;  $q$  equal to two and  $r$  equal to zero; and,  $q$  equal to zero and  $r$  equal to two.

Effects of bis(4-methylpyridine)boronium cation and iodide anion. The influence of iodide ion on reaction was investigated by comparing the rate of the reaction of a solution of 0.50 M 4-methylpyridine-borane, 0.50 M 4-methylpyridine-iodoborane, and 0.10 M triethylammonium iodide with that of a control sample with no triethylammonium iodide under identical conditions. Likewise, the influence of the boron cation was investigated using a solution of 0.50 M 4-methylpyridine-borane, 0.50 M 4-methylpyridine-iodoborane, and 0.10 M bis(4-methylpyridine)boronium iodide. The boronium iodide used here and in subsequent experiments was prepared by reaction 44 as described above for Method B. All three solutions were reacted in capped nmr tubes at 22.0°C for 18 hr, and then  $^1\text{H}$  nmr spectra were taken. The concentrations of unreacted pyridine-borane and 4-methylpyridine-iodoborane were determined for each sample by integration of the 3,5-aromatic resonances of the reactants and the boronium iodide formed. Within experimental error ( $\pm 0.005$  M), the concentrations of unreacted 4-methylpyridine-borane

Table 12  
Second Order Rate Constants for Bis(4-methylpyridine)boronium Iodide  
Formation in Benzene at 70.0°C

Sample <sup>a</sup>	[4-CH <sub>3</sub> pyBH <sub>3</sub> ]	[4-CH <sub>3</sub> pyBH <sub>2</sub> I] O	$k_2, M^{-1} \text{ sec}^{-1}$ $\times 10^4$ for $q = r = 1$	$k_2, M^{-1} \text{ sec}^{-1}$ $\times 10^4$ for $q = 2, r = 0$	$k_2, M^{-1} \text{ sec}^{-1}$ $\times 10^4$ for $q = 0, r = 2$
1	0.250	0.250	2.19	2.19	2.19
2	0.250	0.125	2.26	1.05	4.98
3	0.125	0.250	2.74	6.03	1.23

<sup>a</sup> All reaction times were 100.0 min

were identical in each sample (0.41 M).

Effect of diborane. A 0.80 ml portion of a freshly prepared solution of 0.50 M 4-methylpyridine-borane and 0.50 M 4-methylpyridine-iodoborane in methylene chloride was syringed into a nmr tube fused to a socket joint. The tube was connected to a ball joint-vacuum stopcock-ball joint adapter, and was immediately removed from the Dri-Lab and immersed in liquid nitrogen to freeze the solution. The apparatus was then connected to the vacuum line and evacuated thoroughly, and freshly purified diborane (0.042 mmoles) was condensed into the tube. The quantity of diborane used was 21% of the amount that could be produced by complete reaction according to equation 44. The nmr tube was sealed, warmed to 22.0°C, and  $^1\text{H}$  nmr spectra were taken periodically. The concentrations of reactants remaining at each time were determined by integration of the 3,5-aromatic resonances of the reactants and of the boronium iodide product. A plot of concentration of unreacted borane vs. time is presented in Figure 40 along with a similar plot for a control sample with no externally added diborane. The initial rate for each reaction was determined from the slope of a tangent to the concentration vs. time plot. The solution with the added diborane reacted with an initial rate 0.24 times that of the control sample.

Order with respect to diborane. The reaction was run in a mixed solvent system containing a molar ratio of 2.3 parts of 1,1,2,2-tetrachloroethane for every 1.0 parts of

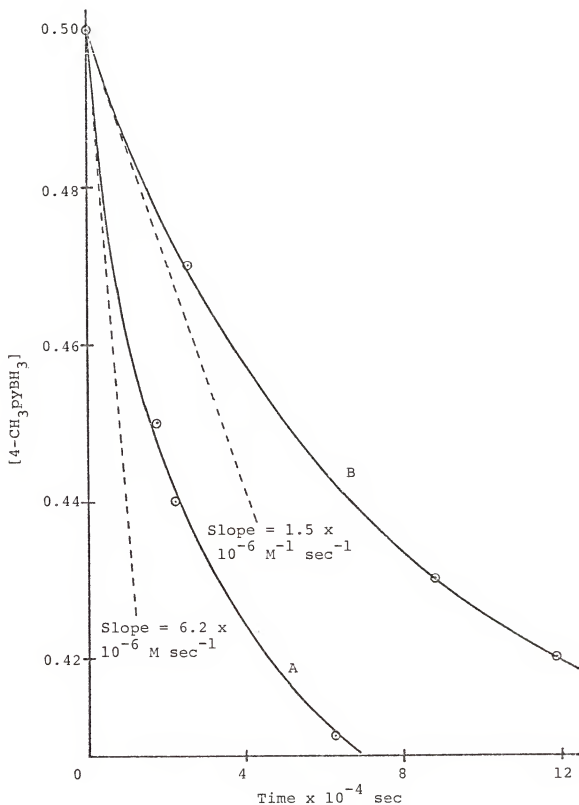


Figure 40. Concentration of 4-methylpyridine-borane vs. time plots for the formation of bis(4-methylpyridine)boronium iodide in methylene chloride at 22°C. Sample B contained 21 mole % of externally added diborane.

1,3,5-trimethylbenzene. This solvent system was suitable for solvation of the boronium iodide formed, and also for adequate resolution of the aromatic  $^1\text{H}$  nmr resonances of the reactants and product. Neither solvent alone exhibits both of these properties. A solution 0.500 M in each reagent was prepared by dissolving 4-methylpyridine-borane (0.5348 g, 5.000 mmole) in approximately 3 ml of dry solvent in a 5 ml volumetric flask. The solution was cooled to approximately  $-10^\circ\text{C}$  (Minifreezer), and solid iodine (0.3173 g, 1.250 mmole) was added a portion at a time while keeping the solution cool. The resulting solution was brought to volume with solvent, and a 0.70 ml sample was pipetted into a special large volume nmr tube. The tube had been expanded near the top to give a spherical bulb, with a constriction between the bulb and a socket joint fused to the open end of the tube. Another sample (3.28 ml) was pipetted into a thick-walled test tube with a standard taper female joint. Both sample tubes were fitted with vacuum stopcock adapters, removed from the Dri-Lab, cooled immediately to  $-196^\circ\text{C}$ , and connected to the vacuum line. The evacuated nmr tube was sealed at the constriction to provide a total volume calibrated to be 8.50 ml. The evacuated test tube was fitted to a calibrated portion of the vacuum line including a manometer. The total volume of the test tube plus manifold (39.8 ml) was kept constant during the reaction by adjusting the mercury level in the manometer as necessary. The vacuum

test tube and manifold were a simulation of the sealed nmr tube with the same ratio of liquid volume to gas volume, and the same relative area for the liquid-gas interface. Consequently, the vacuum test tube provided a model of the large volume nmr tube attached to a manometer, so that  $^1\text{H}$  nmr spectra and pressure measurements could be made on identical systems. Both tubes were immersed in a  $20.0^\circ\text{C}$  constant temperature bath at time zero. Pressure readings of the vacuum line sample and  $^1\text{H}$  nmr spectra of the sealed sample were taken periodically. The temperature of the spectrophotometer probe was equilibrated at  $20^\circ\text{C}$  before insertion of the sample tube. A special large volume pressure cap was required for use with the oversized nmr tube. The concentration of 4-methylpyridine-borane remaining at each time (t) was determined by direct integration of the relative areas of the 3,5-aromatic resonances of the reactants and product. The direct pressure readings of the vacuum line sample were compensated for the vapor pressure of the solvent at  $20.0^\circ\text{C}$  (4.0 mm) to determine the partial pressure of diborane. Figure 41 is a plot of the concentration of 4-methylpyridine-borane vs. time, and Figure 42 is a plot of the pressure of diborane vs. time. Tangents were drawn at several points along the concentration vs. time plot in Figure 41, and their slopes (V) were determined. The concentration and time coordinates of each of these points, and the slopes of the tangents are recorded in Table 13. The corresponding pressure of diborane at each time listed in

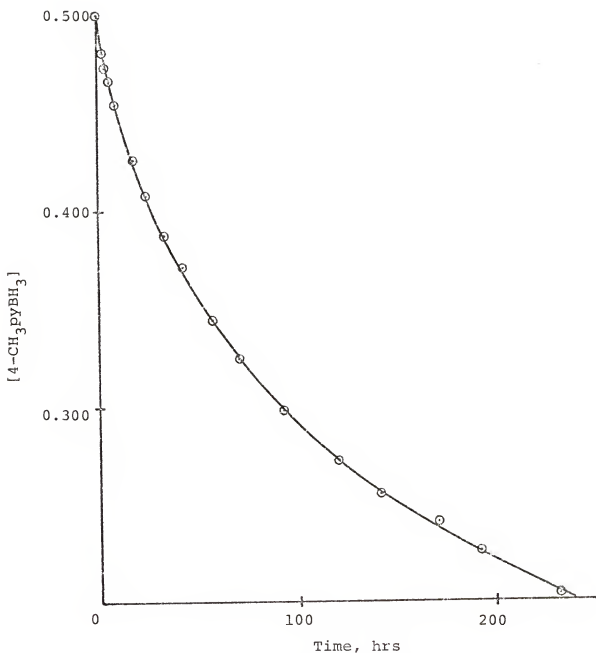


Figure 41. Concentration of 4-methylpyridine-borane vs. time plot for the formation of bis(4-methylpyridine)boronium iodide in 1,1,2,2-tetrachloroethane and mesitylene at 20.0°C.

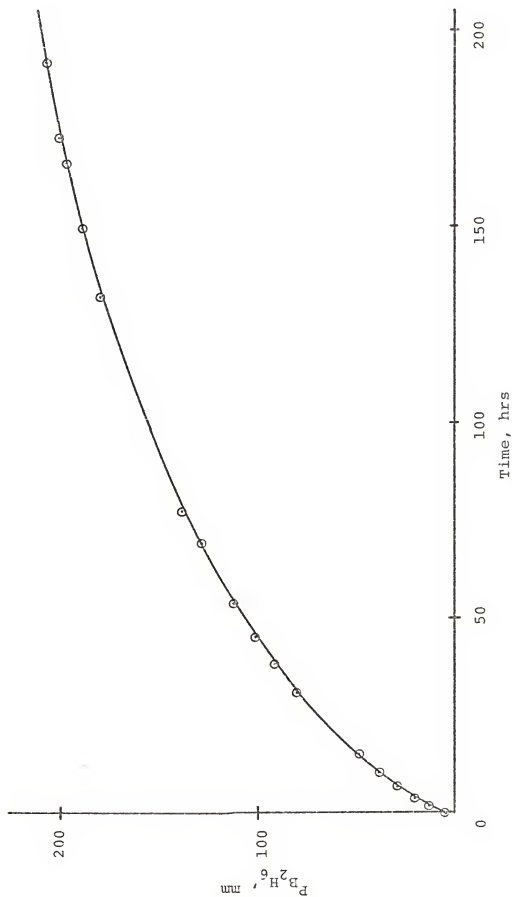


Figure 42. Pressure of diborane vs. time plot for the formation of bis(4-methylpyridine)-boronium iodide in 1,1,2,2-tetrachloroethane and mesitylene at 20.0°C.



Table 13  
Kinetic Data for the Order of Bis(4-methylpyridine)boronium Iodide  
Formation with Respect to Diborane

Time, hr	$V, M^{-1}$ $\frac{hr^{-1}}{10^2} \times$	$[4-CH_3pyBH_3]^a$	$2 + \log \frac{V}{[4-CH_3pyCH_3]^2}$	$P_{B_2H_6}, mm^b$	$3 + \log [B_2H_6]$
5.0	4.40	0.467	0.312	22	0.49
9.0	3.69	0.453	0.256	33	0.60
12.0	3.44	0.443	0.244	40	0.70
28.0	2.26	0.399	0.153	74	0.78
50.0	1.61	0.356	0.116	108	0.85
90.0	1.15	0.303	0.103	149	0.90
130.0	0.83	0.267	0.070	178	0.95
175.0	0.60	0.234	0.042	200	1.04

<sup>a</sup> From Figure 41

<sup>b</sup> From Figure 42

Table 13 was determined from Figure 42, and the concentration of dissolved diborane was calculated from

$$[B_2H_6] = \frac{x}{2} - \frac{\frac{P_{B_2H_6}}{760} V_{\text{gas}}}{RT V_{\text{soln}}} \quad (30)$$

where  $x$  is the concentration of 4-methylpyridine-borane reacted,  $P_{B_2H_6}$  is the pressure of diborane in mm,  $V_{\text{gas}}$  is total volume occupied by diborane in liters for the vacuum line sample,  $R$  is the ideal gas constant,  $T$  is the absolute temperature, and  $V_{\text{soln}}$  is the volume of the vacuum line reaction mixture in liters. A least squares plot of  $2 + \log \frac{V}{[4-CH_3pyBH_3]^2}$  vs.  $3 + \log [B_2H_6]$  was constructed, and the slope was determined (Figure 43).

#### Relative rates of boronium iodide production

Relative rates of boronium iodide production were determined for the 4-methyl, 4-chloro, 2-methyl, 2,6-dimethyl, and unsubstituted pyridine derivatives at 35.0°C in methylene chloride. Solutions 0.50 M each in the pyridine-borane and the respective pyridine-iodoborane were reacted in capped nmr tubes at 35.0°C in a constant temperature bath.  $^1H$  nmr spectra of the samples were taken at various times and after 19 hr of reaction. The extent of reaction after 19 hr was determined for each derivative by integration of the  $^1H$  nmr spectrum at that time. Except for 4-chloro substitution, resonances of the reactants were integrated relative to those of the bis(pyridine)boronium iodide formed. For the methyl-substituted derivatives, the aliphatic region of the

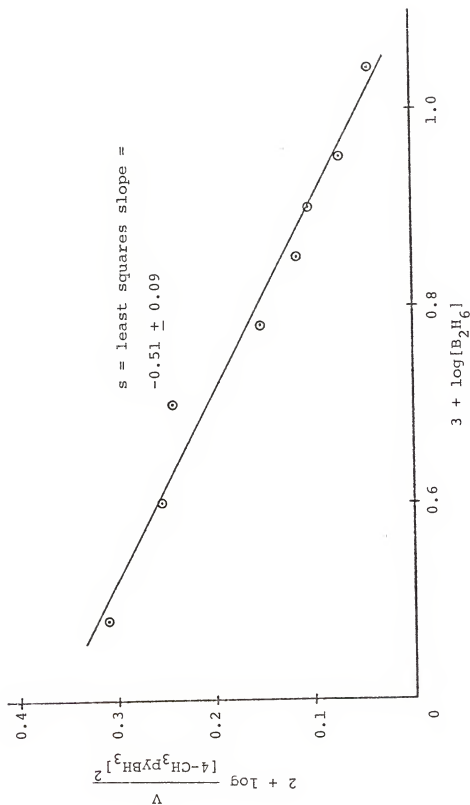


Figure 43. Plot to determine the order with respect to diborane of the reaction to form bis(4-methylpyridine)boronium iodide in 1,1,2,2-tetrachloroethane and mesitylene at 20.0°C.

spectrum was integrated to determine the concentrations of the reactants and the boronium iodide. For 4-methyl and 2-methyl substitution, it was necessary to integrate a 50 Hz sweep width spectrum with a planimeter. For the unsubstituted system, the extent of reaction was determined by integration of the aromatic resonances of the reactants and product. Due to the low solubility of the boronium iodide for 4-chloro substitution, the reaction was monitored by integration of the 2,6-aromatic proton resonances of the reactants vs. n-heptane as a quantitative internal standard. The results are presented in Table 14. The error limits are based on estimates of the accuracy of the nmr integrations.

#### Corroborative Experiments

##### NMR Spectra of Pyridine-Boranes, Pyridine-Iodoboranes, and their Mixtures

##### <sup>1</sup>H nmr spectra

Solutions of substituted pyridine-boranes ( $R\text{-pyBH}_3$ ;  $R=\text{H}$ , 4- $\text{CH}_3$ , 4- $\text{Cl}$ , 2- $\text{CH}_3$ , 2,6- $(\text{CH}_3)_2$ , and 2- $\text{C}(\text{CH}_3)_3$ ), and separate solutions of their monoiodinated derivatives ( $R\text{-pyBH}_2\text{I}$ ) were prepared in methylene chloride and their <sup>1</sup>H nmr spectra were taken (Tables 15 - 17). In addition, spectra were taken for freshly prepared equimolar mixtures of the borane and iodoborane adducts for each pyridine derivative (Figures 44 - 49). The pyridine-iodoborane solutions and the mixtures were prepared in the Dri-Lab by the addition of an appropriate amount of iodine to a solution of

Table 14  
Extents of Bis(pyridine)boronium Iodide  
Formation for Substituted Pyridines  
in Methylene Chloride at 35°C

R in R-py <sup>a</sup>	% Reaction <sup>b</sup>
H	40 $\pm$ 2
4-CH <sub>3</sub>	29 $\pm$ 2
4-Cl	58 $\pm$ 1
2-CH <sub>3</sub>	20 $\pm$ 3
2,6-(CH <sub>3</sub> ) <sub>2</sub>	4.6 $\pm$ 0.5

<sup>a</sup> [R-pyBH<sub>3</sub>]<sub>0</sub> = [R-pyBH<sub>2</sub>I]<sub>0</sub> = 0.50

<sup>b</sup> All reaction times were 19 hr

Table 15  
<sup>1</sup>H NMR Data for Substituted Pyridine-Boranes

R <sup>a</sup> in R-py	δCH <sub>3</sub> (Hz), m <sup>b</sup>	δH <sub>3,5</sub> (Hz), m <sup>b</sup> (J) <sup>c</sup>	δH <sub>4</sub> (Hz), m <sup>b</sup>	δH <sub>2,6</sub> (Hz), m <sup>b</sup> (J) <sup>c</sup>
H	---	450 M	478 M	513 D (6)
4-CH <sub>3</sub> <sup>d</sup>	148 S	438 D (6)	----	503 D (6)
4-Cl	----	450 D (7)	----	508 D (7)
2-CH <sub>3</sub>	162 S	439 M (6)	471 M	522 D (6)
2,6-(CH <sub>3</sub> ) <sub>2</sub>	165 S	433 M	460 M	----
2-C(CH <sub>3</sub> ) <sub>2</sub>	97 S	450 M	450 M	529 D (6)

<sup>a</sup> 0.5 M - 1.0 M in methylene chloride

<sup>b</sup> Multiplicities (m) are given as S = singlet, D = doublet, and M = complex multiplet

<sup>c</sup> Coupling constants (J) are in Hz

<sup>d</sup> The data for spectrum of a solution in 1,1,2,2-tetrachloroethane are essentially identical

Table 16  
<sup>1</sup>H NMR Data for Substituted Pyridine-Iodoboranes

R <sup>a</sup> in R-py	$\delta\text{CH}_3$ (Hz), m <sup>b</sup>	$\delta\text{H}_{3,5}$ (Hz), m <sup>b</sup> , (J) <sup>c</sup>	$\delta\text{H}_4$ (Hz), m <sup>b</sup>	$\delta\text{H}_{2,6}$ (Hz), m <sup>b</sup> , (J) <sup>c</sup>
H	----	462 M	493 M	528 D (5)
4-CH <sub>3</sub> <sup>d</sup>	151 S	447 D (7)	----	518 D (7)
4-Cl	----	459 D (7)	----	524 D (7)
2-CH <sub>3</sub>	171 S	447 M	484 M	525 D (6)
2,6-(CH <sub>3</sub> ) <sub>2</sub>	172 S	441 M	472 M	----
2-C(CH <sub>3</sub> ) <sub>2</sub>	97 S, 98 1/2 S	480 M	480 M	543 D (6)

<sup>a</sup> 0.5 M - 1.0 M in methylene chloride

<sup>b</sup> Multiplicities (m) are given as S = singlet, D = doublet, and M = complex multiplet

<sup>c</sup> Coupling constants (J) are in Hz

<sup>d</sup> The data for a spectrum of a solution in 1,1,2,2-tetrachloroethane are essentially identical

Table 17  
<sup>1</sup>H NMR Chemical Shifts for the Methyl Resonances of  
 Alkyl-Substituted Pyridine-Boranes, Pyridine-Iodoboranes,  
 and their Mixtures

R in R-py	$\delta\text{CH}_3$ for R-pyBH <sub>3</sub> (Hz) <sup>a</sup>	$\delta\text{CH}_3$ for R-pyBH <sub>2</sub> I (Hz) <sup>a</sup>	Expected $\Delta\delta_{\text{CH}_3}$ (Hz) <sup>b</sup>	Found $\Delta\delta_{\text{CH}_3}$ (Hz)	$\delta\text{CH}_3$ for Mixture
4-CH <sub>3</sub> <sup>d</sup>	148	151	3	0	149 1/2
2-CH <sub>3</sub>	162	171	9	4	169, 165
2,6-(CH <sub>3</sub> ) <sub>2</sub>	165	172	7	0	169

<sup>a</sup> 0.50 - 1.0 M in methylene chloride

<sup>b</sup>  $\Delta\delta_{\text{CH}_3}$  = difference in chemical shifts of the borane adduct and the corresponding iodoborane adduct

<sup>c</sup> [R-pyBH<sub>3</sub>] = [R-pyBH<sub>2</sub>I] = 0.50 - 1.0 in methylene chloride

<sup>d</sup> The data for a spectrum of a solution in 1,1,2,2-tetrachloroethane are essentially identical



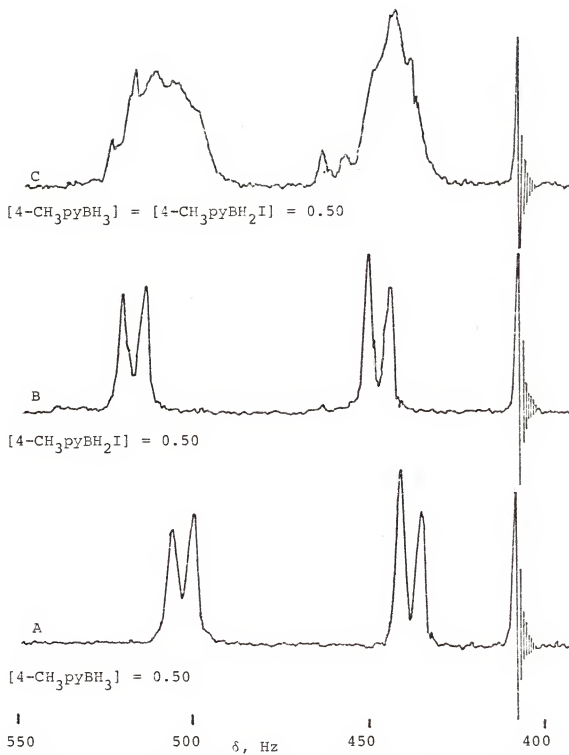


Figure 44.  $^1\text{H}$  nmr spectra of 4-methylpyridine adducts in methylene chloride.

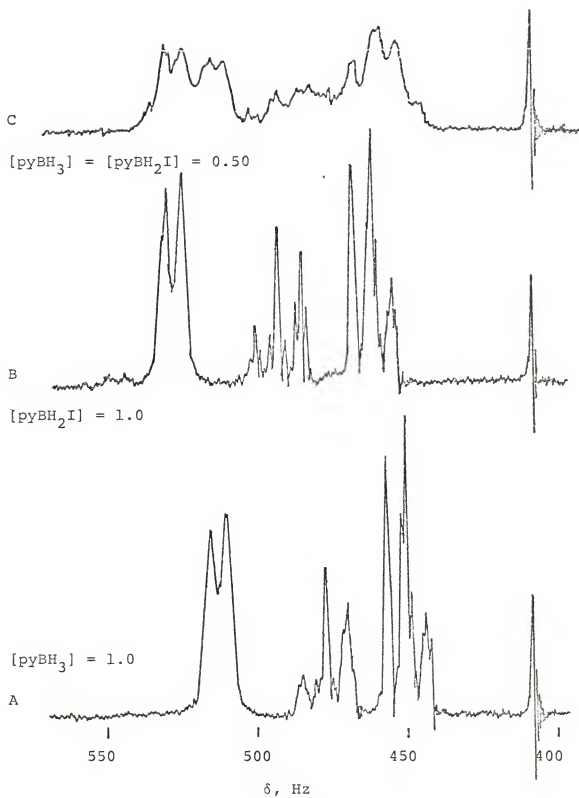


Figure 45.  $^1\text{H}$  nmr spectra of pyridine adducts in methylene chloride.

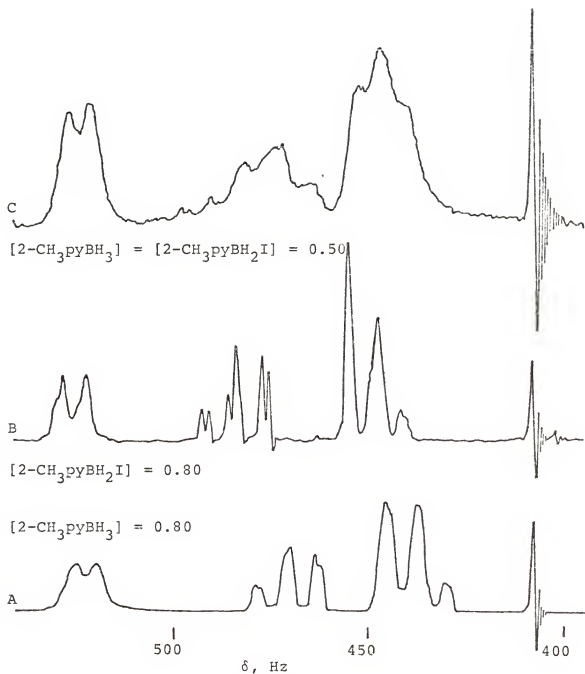


Figure 46.  $^1\text{H}$  nmr spectra of 2-methylpyridine adducts in methylene chloride.

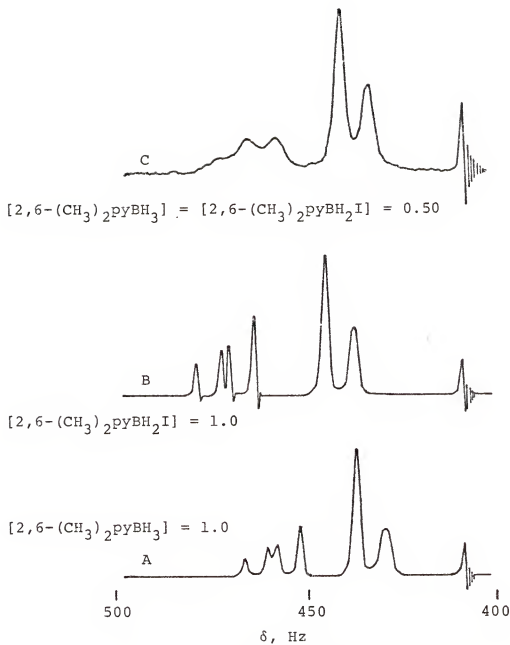


Figure 47.  $^1\text{H}$  nmr spectra of 2,6-dimethylpyridine adducts in methylene chloride.

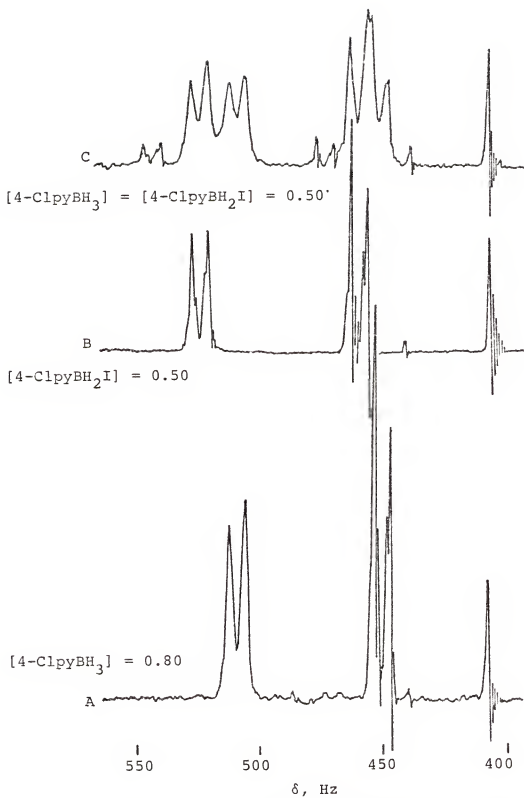


Figure 48.  $^1\text{H}$  nmr spectra of 4-chloropyridine adducts in methylene chloride.

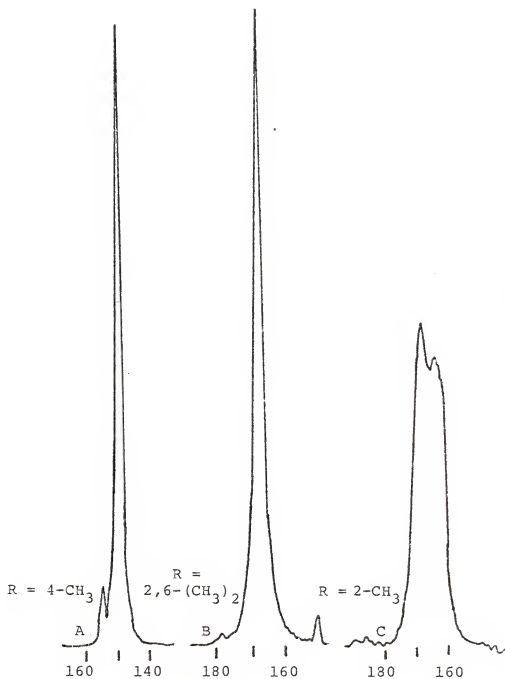


Figure 49. Aliphatic resonances in the  $^1\text{H}$  nmr spectra of equimolar mixtures of alkyl-substituted pyridine-boranes and pyridine-iodoboranes in methylene chloride;  $[\text{R-pyBH}_3] = [\text{R-pyBH}_2\text{I}] = 0.50$ .

the pyridine-borane as described previously.

Effect of tetra(n-butyl)ammonium iodide. The influence of iodide ion on the  $^1\text{H}$  nmr spectrum of a mixture of a substituted pyridine-borane and the corresponding pyridine-iodoborane was investigated for a solution containing 0.500 M 4-methylpyridine-borane, 0.500 M 4-methylpyridine-iodoborane, and 1.02 M tetra(n-butyl)ammonium iodide in methylene chloride. The features of the  $^1\text{H}$  nmr spectrum of the resulting solution were essentially identical to those of an analogous solution without the ammonium iodide (Figures 44-C and 49-A).

Effect of diborane. The preparation of a sample of 4-methylpyridine-borane and 4-methylpyridine-iodoborane with added diborane was described previously (p 91). The general features of the  $^1\text{H}$  nmr spectrum of the solution after 1 hr at room temperature were the same as those of an otherwise identical solution with no externally added diborane (Figure 44-C) except that a lower concentration of the bis(4-methylpyridine)boronium iodide was observed for the sample containing added diborane.

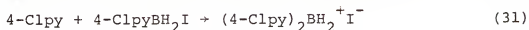
Temperature effects. A portion of a cold ( $-10^\circ\text{C}$ ), freshly prepared solution of 0.50 M 4-methylpyridine-borane and 0.50 M 4-methylpyridine-iodoborane in 1,1,2,2-tetrachloroethane was placed in a nmr tube fused to a socket joint. The tube was connected to a ball joint/vacuum stopcock/ball joint adapter, removed from the Dri-Lab, and placed in liquid nitrogen. The apparatus was then attached to the vacuum line and evacuated before sealing the frozen sample

in the tube. The sealed tube was placed in the precooled probe of the spectrophotometer, and the  $^1\text{H}$  nmr spectrum was taken after equilibration at  $-48^\circ\text{C}$ . Spectra were also taken at progressively higher temperatures up to  $+16^\circ\text{C}$  (Figures 50 and 51). A small, very broad peak centered at approximately 200 Hz was also visible at low temperature.

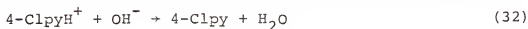
### $^{11}\text{B}$ nmr spectra

Solutions of 1.0 M 4-methylpyridine-borane, 1.0 M 4-methylpyridine-iodoborane, and a mixture of 1.0 M 4-methylpyridine-borane and 1.0 M 4-methylpyridine-iodoborane were prepared in the methylene chloride, and their  $^{11}\text{B}$  nmr spectra were obtained. The results are presented in Figure 52. The spectrum of the mixture was obtained on a freshly prepared sample.

### Preparation of Bis(4-chloropyridine)boronium Iodide from 4-Chloropyridine and 4-Chloropyridine-Iodoborane



The method of Ryschkewitsch<sup>49,50</sup> for the preparation of bis(amine)boronium iodides from the reaction of amines with amine-iodoboranes was employed. Since 4-chloropyridine is unstable,<sup>51</sup> it was necessary to prepare a fresh aqueous solution of the free amine from its hydrochloride salt.



4-Chloropyridine hydrochloride (7.50 g, 50.0 mmole) was dissolved in 25 ml of distilled water, and a sodium hydroxide



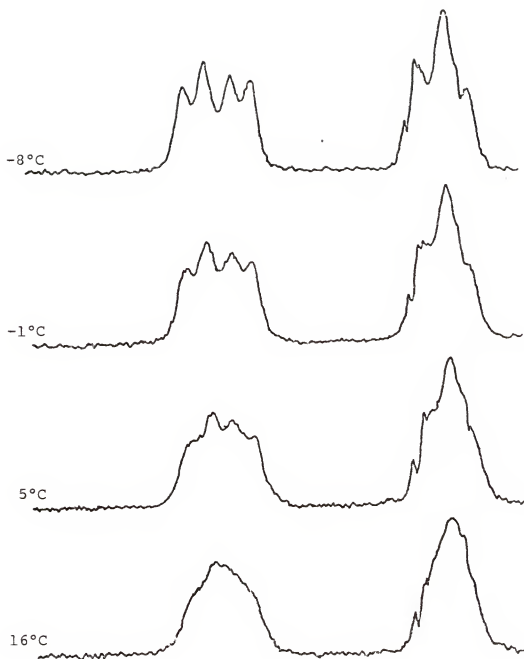


Figure 50. Temperature dependence of the aromatic region of the  $^1\text{H}$  nmr spectrum of an equimolar mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in 1,1,2,2-tetrachloroethane.

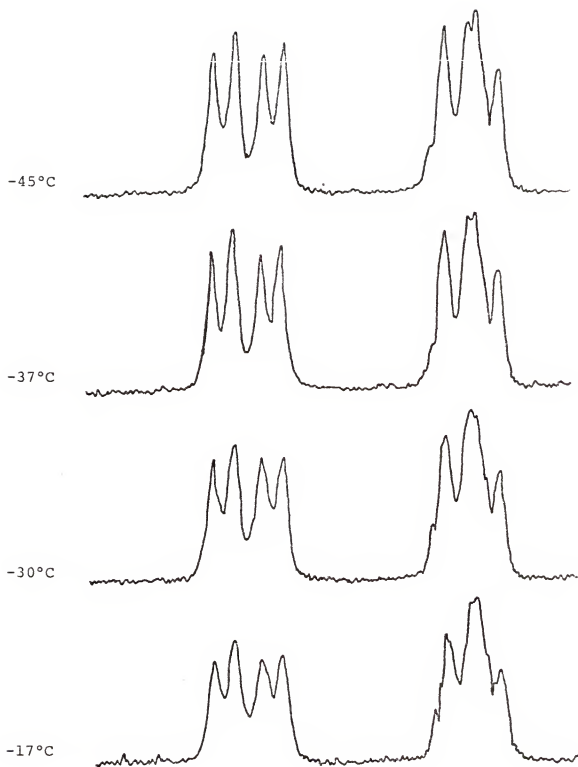


Figure 50 continued.

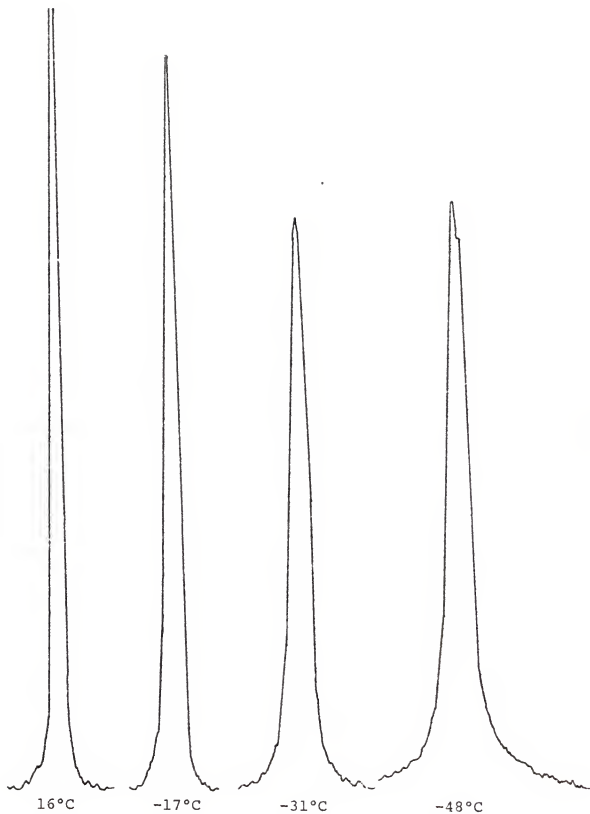


Figure 51. Temperature dependence of the aliphatic region of the  $^1\text{H}$  nmr spectrum of an equimolar (0.50 M) mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in 1,1,2,2-tetrachloroethane.

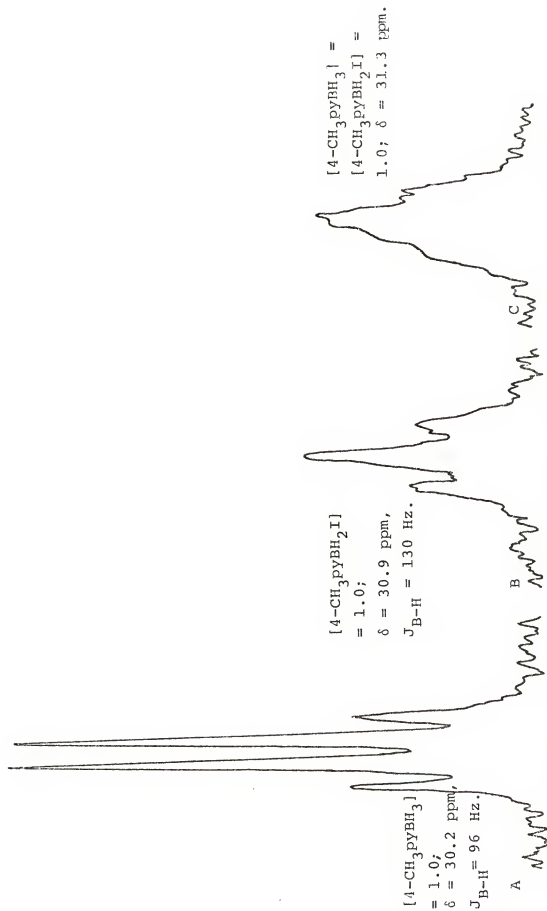


Figure 52.  $^{11}\text{B}$  nmr spectra of 4-methylpyridine adducts in methylene chloride.

solution\* (50.0 ml of 1.00 M) was added a drop at a time with stirring. As the sodium hydroxide was added the solution became yellow, and after the addition was half complete a yellow layer formed. The mixture was extracted with 80 ml of benzene, and the colorless, turbid organic layer was stirred over anhydrous magnesium sulfate for 10 min, and then over calcium hydride for 18 hr to remove water. The mixture was filtered and washed with benzene, and an aliquot of the clear filtrate was standardized with 0.100 M HCl to a methyl orange endpoint to determine the 4-chloropyridine concentration (0.465 M). Next a 77.0 ml portion of the standardized 4-chloropyridine solution (2% excess) was reacted with 34.0 mmole of 4-chloropyridine-iodoborane dissolved in 75 ml of benzene. The iodoborane was prepared in situ from the reaction of 4-chloropyridine-borane (4.33 g, 34.0 mmole) with iodine (4.32 g, 17.0 mmole). The 4-chloropyridine solution was added dropwise over a 1 hr period. The bis(4-chloropyridine)boronium iodide which precipitated was filtered, washed with benzene, and dried under vacuum (12.2 g, 98.0% yield). The infrared spectrum of the product contained the following adsorptions ( $\text{cm}^{-1}$ ): 3090 (med,s), 3060 (st,s), 3040 (wk,s), 3000 (wk,s), 2500 (med,s), 2460 (wk,s), 1612 (st,s), 1560 (v wk), 1480 (st,s), 1430 (st,s), 1380 (v wk), 1353 (v wk), 1265 (med,s), 1200 (med,s), 1150 (st,s), 1130 (v wk), 1120

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\*It is important not to use a large excess of sodium hydroxide over the quantity required by equation 32. No 4-chloropyridine could be isolated from reaction mixtures containing large (100%) excesses of NaOH.

(sh), 1100 (sh), 1085 (st,s), 1075 (sh), 1050 (med,s), 960 (v wk), 905 (wk,s), 859 (wk,s), 845 (wk,s), 835 (st,s), 782 (st,s), 740 (wk,s), 660 (v wk), 630 (v wk), 520 (med,s), and 495 (med,s). The boronium iodide is insoluble in acetonitrile, nitromethane, and acetone, and slightly soluble in water and methylene chloride. The compound is moderately soluble in methanol, but apparently undergoes slow solvolysis with gas evolution and formation of a green solution. The  $^1\text{H}$  nmr spectrum of the crude boronium iodide in methanol consisted of two doublets ( $J=7$ ) 482 Hz and 533 Hz, with no detectable resonances due to impurities. The boronium iodide was converted to the hexafluorophosphate salt by the method of Nainan and Ryschkewitsch.<sup>52</sup> The yield of the conversion was only 82.9%, presumably due to the large quantities of water required to dissolve the iodide salt. The boronium hexafluorophosphate is insoluble in methylene chloride, and soluble in acetonitrile. The infrared spectrum of the compound contained the following absorptions ( $\text{cm}^{-1}$ ): 3120 (wk,s), 3100 (sh), 2520 (sh), 2485 (med,s), 2430 (wk,s), 2390 (v wk), 1616 (st,s), 1563 (med,s), 1492 (med,s), 1462 (v wk), 1438 (st,s), 1262 (wk,s), 1198 (wk,s), 1165 (sh), 1155 (st,s), 1132 (wk,s), 1103 (sh), 1090 (st,s), 1075 (sh), 1056 (med,s), 1020 (v wk), 882 (sh), 860 (st,s), 833 (st,s), 825 (sh), 782 (med,s), 743 (wk,s), 663 (v wk), 557 (st,s), 523 (med,s), 498 (med,s), and 387 (v wk). The spectrum of the compound was unchanged after recrystallization from acetonitrile with

ether. The  $^1\text{H}$  nmr spectrum of an acetonitrile solution of the recrystallized boronium hexafluorophosphate consisted of two doublets ( $J=7$ ) at 474 and 519 Hz, with no other resonances detectable. Elemental analysis of the recrystallized cation gave the following results:

C=31.37%, H=2.67%, N=7.27%, B=3.06%, and Cl=18.27%;

theory for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{BCl}$ :

C=31.21%, H=2.62%, N=7.28%, B=2.81%, and Cl=18.42%.

Identification of Diborane and Bis(4-chloropyridine)boronium Iodide as Products of the Reaction Between 4-Chloropyridine-Borane and 4-Chloropyridine-Iodoborane; Stoichiometry of the Reaction

4-Chloropyridine-borane (2.55 g, 20.0 mmole) was dissolved in 100 ml of dry benzene in the Dri-Lab in a 500 ml 2-neck flask fitted with a vacuum stopcock adapter and a tipping tube containing iodine (1.27 g, 5.00 mmole). The apparatus was removed from the Dri-Lab, connected to the vacuum line, and evacuated to a pressure of 110 mm. As the iodine was added to the reaction flask over a 1 hr period, a yellow precipitate formed. Then the reaction mixture was frozen, and the flask was evacuated through two cold traps at  $-78^\circ\text{C}$ , and then through two others at  $-196^\circ\text{C}$ . The flask was warmed to room temperature and the reaction mixture was stirred. Periodically, volatile portions were removed from the reaction flask and were fractionated through the  $-78^\circ\text{C}$  and  $-196^\circ\text{C}$  traps. The material condensing at  $-78^\circ\text{C}$  was returned to the reaction flask, and the material condensing at  $-196^\circ\text{C}$  was kept frozen. After several weeks of reaction,

the mixture was evacuated to dryness through the series of traps. The material condensing at  $-196^{\circ}\text{C}$  was distilled four times through a  $-130^{\circ}\text{C}$  trap (n-pentane slush) to remove traces of benzene. The infrared spectra of the contents of the  $-78^{\circ}\text{C}$  and  $-130^{\circ}\text{C}$  traps showed the presence of benzene only.

#### Characterization of diborane

The infrared spectrum (42 mm pressure) and mass spectrum of the gas condensing at  $-196^{\circ}\text{C}$  were identical to the published spectra of diborane.<sup>53</sup> The gram molecular weight of the gas was determined as 27.2 g/mole (theory=27.6 g/mole for  $\text{B}_2\text{H}_6$ ). A total of 3.81 mmole of diborane was obtained (76.2% yield), although some losses occurred due to leakage into the vacuum system on long standing.

#### Characterization of bis(4-chloropyridine)boronium iodide and hexafluorophosphate

The nonvolatile residue from the reaction mixture was slurried with 50 ml of benzene and filtered in the Dri-Lab. The yellow, insoluble solid was washed with benzene and dried under vacuum to a constant weight of 3.27 g. The infrared spectrum of the solid was identical to that of the bis(4-chloropyridine)boronium iodide prepared from the reaction of 4-chloropyridine with 4-chloropyridine-iodoborane, except for a medium, sharp absorption at  $1558\text{ cm}^{-1}$  in the former spectrum. Further the  $^1\text{H}$  nmr spectrum of the compound dissolved in methanol was identical to that of the bis(4-chloropyridine)-boronium iodide prepared by the reaction of the free amine



with the amine-iodoborane. The weight of the boronium iodide collected corresponded to an 89.2% yield. The weight of the benzene-soluble portion of the nonvolatile residue from the reacture mixture was 0.52 g. The theoretical weight for the unreacted 4-chloropyridine-borane and 4-chloropyridine-iodoborane was 0.43 g.

The bis(4-chloropyridine)boronium iodide was converted to the hexafluorophosphate salt<sup>52</sup> with an 86.3% yield. The infrared spectrum of the compound was identical to that of the boronium hexafluorophosphate prepared by the method of Ryschkewitsch,<sup>49,50</sup> but the  $^1\text{H}$  nmr spectrum ( $\text{CH}_3\text{CN}$ ) exhibited a minor resonance at 497 Hz due to an impurity in addition to the peaks expected for the product. Recrystallization of the boronium hexafluorophosphate from acetonitrile with ether eliminated most of the impurity detected in the  $^1\text{H}$  nmr spectrum. Elemental analysis of the recrystallized cation gave the following results:

C=30.98%, H=2.54%, N=6.94%, B=3.00%, and Cl=18.68%;  
theory for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{BCl}_2$ :

C=31.21%, H=2.62%, N=7.28%, B=2.81%, and Cl=18.42%.

Melting points and mixed melting points of the bis(4-chloropyridine)boronium hexafluorophosphates. The melting points of the bis(4-chloropyridine)boronium hexafluorophosphates prepared by the reaction of 4-chloropyridine with 4-chloropyridine-iodoborane, and by the reaction of 4-chloropyridine-borane with 4-chloropyridine-iodoborane were deter-

mined. The melting point of the compound prepared by the former method was 128.5-129.2°C, and that of the compound prepared by the latter method was 128.2-128.5°C. A ground 50/50 mixture of the two hexafluorophosphates melted at 128.3-128.5°C. All three melting points were determined simultaneously in an oil bath heated at 2°C per minute. The boronium hexafluorophosphate melts with decomposition with the formation of a gas and a green liquid. Consequently, the observed melting point of a given sample is quite dependent on the rate of heating, so that simultaneous heating of different samples is desirable for comparison purposes. Sharp melting points as high as 144.3-145.0°C could be obtained for the above samples by heating at a faster rate.

Reactions of 4-Chloropyridine-Borane and 4-Chloropyridine-Iodoborane in Methylene Chloride

Reaction of 4-chloropyridine-borane with 4-chloropyridine-iodoborane

A solution containing 0.50 M 4-chloropyridine-borane and 0.50 M 4-chloropyridine-iodoborane in methylene chloride was stirred in a stoppered test tube for 64 hr at room temperature. The yellow precipitate which formed was filtered, washed with methylene chloride, and dried under vacuum. The dried weight of the solid corresponded to a 51% yield of bis(4-chloropyridine)boronium iodide. The boronium iodide was converted to the hexafluorophosphate<sup>52</sup> salt with an overall yield of 45%. Except for a very weak absorption at 638  $\text{cm}^{-1}$ , the infrared spectrum of the compound was identical to

that of an analyzed sample of the boronium hexafluorophosphate. Likewise, the  $^1\text{H}$  nmr spectrum in acetonitrile and solubility properties of the compound were identical to those of analyzed bis(4-chloropyridine)boronium hexafluorophosphate.

#### Reaction of 4-chloropyridine-borane

A 0.50 M solution of 4-chloropyridine-borane in methylene chloride, reacted under the same conditions as the mixture above (64 hr at room temperature), failed to produce any boronium iodide. The  $^1\text{H}$  nmr spectrum of the solution was unchanged and no precipitate was formed.

#### Reaction of 4-chloropyridine-iodoborane

A 0.50 M solution of 4-chloropyridine-iodoborane stirred for 64 hr at room temperature in a stoppered test tube failed to produce any boronium iodide. The  $^1\text{H}$  nmr spectrum of the solution showed no change and no precipitate was formed.

#### Isolation of the Bis(4-chloropyridine)boronium Cation from the Reaction of Trimethylamine-Iodoborane with 4-Chloropyridine-Borane

A solution of 1.0 M 4-chloropyridine-borane and 1.0 M trimethylamine-iodoborane in methylene chloride was reacted at room temperature. After 1 hr, the solution was yellow and a yellow crystalline precipitate had formed.\* Continued reaction produced more solid. After 2 days, the reaction mixture was filtered, and the solid was washed with methylene

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\*In other experiments under similar conditions, considerably longer times were required for precipitation of the product.

chloride and dried under vacuum. The infrared spectrum of the precipitate was identical to that of the bis(4-chloropyridine)boronium iodide prepared by the reaction of 4-chloropyridine with 4-chloropyridine-iodoborane except for a very small unidentified peak at  $1710\text{ cm}^{-1}$ . The solid, which was slightly soluble in water, was converted to the hexafluorophosphate salt.<sup>52</sup> The  $^1\text{H}$  nmr and infrared spectra of the compound were identical to those of an analyzed sample of the bis(4-chloropyridine)boronium hexafluorophosphate, except for a small absorption at  $630\text{ cm}^{-1}$  in the latter spectrum.

Reaction of 4-Methylpyridine-Borane and 4-Methylpyridine-Iodoborane

Iodine (0.635 g, 2.50 mmole) was added to a stirred solution of 4-methylpyridine-borane (1.07 g, 10.0 mmole) in 20 ml of benzene, and the flask was removed from the Dri-Lab and fitted to a reflux condenser. A flow of nitrogen was passed across the top of the condenser to carry volatile materials from the reaction mixture through a bubbler containing a solution of 4-methylpyridine in benzene. The reaction mixture was heated for 11 hr at  $70^\circ\text{C}$ , cooled to room temperature, and the white precipitate (0.829 g) was filtered and washed with benzene in the Dri-Lab. Further heating of the filtrate for 18 hr at  $80^\circ\text{C}$  produced another 0.587 g of precipitate. The infrared and  $^1\text{H}$  nmr spectra ( $\text{CH}_2\text{Cl}_2$ ) of each batch of precipitate were identical to those of an analyzed sample of the bis(4-methyl)pyridineboronium iodide.

The weight of solid collected corresponded to a 86.9% yield, with another 7.0% of unprecipitated product suggested by the  $^1\text{H}$  nmr spectrum of the final filtrate. The evolution of diborane as a reaction product was deduced by the isolation of 4-methylpyridine-borane from the trap containing 4-methylpyridine. The compound so collected exhibited a  $^1\text{H}$  nmr spectrum identical to that of 4-methylpyridine-borane, and had a melting point of 73.6-73.9°C (lit. 72-73°C<sup>54</sup>).

#### Reaction of Trimethylamine-Borane with Trimethylamine-Iodoborane

A solution containing 1.0 M trimethylamine-borane and 1.0 M trimethylamine-iodoborane in benzene was refluxed vigorously for 8 days. After cooling to room temperature, the reaction mixture contained only a trace of solid. Neither the solid nor an aqueous extract of the benzene solution yielded any precipitate upon treatment with saturated aqueous ammonium hexafluorophosphate. Further, the  $^1\text{H}$  nmr spectrum of the benzene solution showed no change from its original appearance, so that it was concluded that no bis(trimethylamine)boronium iodide had been formed.

In another experiment, a methylene chloride solution containing 2.50 mmole each of trimethylamine-borane and trimethylamine-iodoborane was evaporated to dryness, and the reaction flask was attached to the vacuum line. After evacuation, the reaction mixture was heated to approximately 60°C in oil bath at which point the solid melted. The molten system was heated to 80-85°C for 14 hr. No diborane was

produced, and the  $^1\text{H}$  nmr spectrum of the residue dissolved in methylene chloride exhibited resonances of the starting materials only. No resonances attributable to bis(trimethylamine)boronium iodide were visible under conditions where 0.2% reaction would be readily detectable.

#### Preparation of 4-Methylpyridine-Trifluoroborane

Freshly distilled 4-methylpyridine (30.0 ml, 307 mmole;  $b\ p = 143.8\text{--}144.0^\circ\text{C}$  at 756 mm) was dissolved in 130 ml of benzene in a 3-neck flask. The flask was flushed with nitrogen, and boron trifluoride was bubbled through the stirred solution until the effluent gas smoked in the air, and then 10 min longer. The reaction mixture was evacuated to dryness, and the white solid residue (49.5%) collected in the Dri-Lab corresponded to a 97.7% yield of 4-methylpyridine-trifluoroborane. The  $^1\text{H}$  nmr spectrum of the crude product dissolved in methylene chloride exhibited only one major methyl resonance with a smaller shoulder attributed to an impurity. Recrystallization of the crude product from benzene removed the impurity. The  $^1\text{H}$  nmr spectrum of the recrystallized adduct dissolved in methylene chloride consisted of a singlet at 154 Hz, and two doublets ( $J=6$  Hz) at 454 and 509 Hz, with the latter resonance broadened. The  $^{19}\text{F}$  nmr spectrum of the compound in methylene chloride consisted of a quartet at 33.5 ppm ( $J_{\text{B-F}}=11.5$  Hz). The infrared spectrum of the compound contained the following absorptions ( $\text{cm}^{-1}$ ): 3120 (wk, s), 3070 (wk, s), 2570 (wk, br), 1970 (v wk), 1870 (v wk),

1660 (sh), 1640 (st,s), 1570 (wk,s), 1510 (med,s), 1451 (med,s), 1380 (wk,br), 1230 (sh), 1220 (sh), 1210 (sh), 1160 (st,s), 1100 (st,br), 1067 (wk,s), 1045 (sh), 960 (sh), 935 (sh), 905 (st,br), 832 (med,s), 800 (sn), 730 (wk,s), 678 (st,s), 560 (med,s), 540 (med,s), 460 (v wk), 372 (wk,s), and 345 (wk,br). Elemental analysis of the adduct gave the following results:

C=44.66%, H=4.10%, N=8.72%, B=6.79%, and F=35.17%;

theory for  $C_6H_7NBF_3$ :

C=44.78%, H=4.38%, N=8.70%, B=6.72%, and F=35.42%.

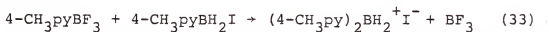
The melting point of the compound was 87-89°C in contrast to a literature report of 65-68°C.<sup>55</sup> Likewise the reported stability of the compound on exposure to air<sup>55</sup> was found to be erroneous.

#### Reaction of 4-Methylpyridine-Trifluoroborane with 4-Methylpyridine-Iodoborane

A solution of 1.0 M 4-methylpyridine-trifluoroborane and 1.0 M 4-methylpyridine-iodoborane in methylene chloride was reacted for 6 hr at room temperature. The  $^1H$  nmr spectrum of the resulting solution was exactly that expected for simple additivity of the spectra for each solute. Further, the  $^{19}F$  nmr spectrum of the solution exhibited only one resonance ( $\delta=33.9$  ppm,  $J_{B-F}=11.5$  Hz) which was attributed to unreacted 4-methylpyridine-trifluoroborane, so that no evidence of ligand-ligand exchange between solutes was apparent.

In another experiment, a 0.33 M solution of 4-methylpyridine-iodoborane was prepared in situ by the reaction of

iodine (1.01 g, 4.00 mmole) with 4-methylpyridine-borane (0.854 g, 8.00 mmole) in 24 ml of benzene. The 4-methylpyridine-boron trifluoride adduct (1.29 g, 8.00 mmole) was added to the solution, and the mixture was refluxed gently for 4 hr. The reaction mixture was cooled to room temperature, and after 12 hr it was filtered in the Dri-Lab. The white solid, which was collected by filtration, was identified as essentially pure bis(4-methylpyridine)boronium iodide by comparison of its  $^1\text{H}$  nmr ( $\text{CH}_2\text{Cl}_2$ ) and infrared spectra with those of an analytically pure sample. Minor absorptions due to an impurity could be seen as a shoulder at 157 Hz in the  $^1\text{H}$  nmr spectrum, and as weak, sharp peaks at  $770\text{ cm}^{-1}$  and  $862\text{ cm}^{-1}$  in the infrared spectrum. The yield of the boronium iodide (0.245 g, 0.751 mmole) was 9.4% based on equation 33.



The  $^1\text{H}$  nmr spectrum of the filtrate from the reaction mixture suggested the presence of another 0.414 mmole (5.2%) of unprecipitated boronium iodide. Further workup of the reaction mixture verified the presence of this quantity of supersaturated boron cation by the quantitative isolation of the bis(4-methylpyridine)boronium hexafluorophosphate from a portion of the filtrate. Thus, the total yield of boronium iodide on 4 hr of heating was 14.6%.

In order to identify the unreacted starting materials, the filtrate was divided quantitatively into two portions.



One portion was evaporated to dryness and the residue was dissolved in methylene chloride. Compensating for the small amount of unprecipitated boronium iodide known to be present in the filtrate, the  $^1\text{H}$  nmr spectrum of the solution was identical to that of a 50/50 mixture of 4-methylpyridine-iodoborane and 4-methylpyridine-trifluoroborane. The  $^{19}\text{F}$  nmr spectrum of the solution contained only a quartet ( $\delta = 33.7$  ppm,  $J_{\text{B-F}} = 11.5$  Hz) attributed to the 4-methylpyridine-boron trifluoride adduct.

Excess 4-methylpyridine was added to the other portion of the filtrate from the reaction mixture to precipitate unreacted 4-methylpyridine-iodoborane as the bis(4-methylpyridine)boronium iodide.<sup>49,50</sup> The mixture was filtered in the Dri-Lab, and the filtrate was retained for the isolation and identification of unreacted 4-methylpyridine-trifluoroborane (vide infra). The material precipitated by the addition of 4-methylpyridine was identified as essentially pure bis(4-methylpyridine)boronium iodide by comparison of its  $^1\text{H}$  nmr ( $\text{CH}_2\text{Cl}_2$ ) and infrared spectra with those of a pure sample. The spectra were identical except for minor absorptions due to an impurity at 160 Hz in the  $^1\text{H}$  nmr spectrum and at  $862\text{ cm}^{-1}$  (wk,s) in the infrared spectrum. The weight of boronium iodide collected corresponded to 86.4% unreacted 4-methylpyridine-iodoborane (theory = 85.3%). The volume of the filtrate was reduced under vacuum and unreacted 4-methylpyridine boron trifluoride was precipitated by the addition

of hexanes. The compound was identified by its  $^1\text{H}$  nmr ( $\text{CH}_2\text{Cl}_2$ ) and infrared spectra, although the former contained a minor resonance due to an impurity at 156 Hz. The weight of compound recovered corresponded to 59.7% unreacted 4-methylpyridine-trifluoroborane.

In comparison experiments, a solution containing 0.33 M 4-methylpyridine-iodoborane in benzene, and a separate solution containing 0.33 M 4-methylpyridine-iodoborane and 0.33 M 4-methylpyridine-borane in benzene were heated under identical conditions as the solution containing the iodoborane and boron trifluoride adducts (above). Subsequent workups isolated 2.8% and 89.2% yields of bis(4-methylpyridine)boronium iodide, respectively. The products were identified as pure boronium iodide by their infrared spectra. The benzene-soluble portion of the amine-iodoborane reaction mixture was evaporated to dryness, and the  $^1\text{H}$  nmr spectrum of the residue dissolved in methylene chloride indicated the presence of unreacted 4-methylpyridine-iodoborane only.

Identification of Supersaturated Bis(4-methylpyridine)boronium Iodide in Benzene

The solubilities of the bis(4-methylpyridine)boronium iodide salt in separate 1.0 M solutions of 4-methylpyridine-iodoborane and 1.0 M 4-methylpyridine-borane in benzene were determined by stirring each solution in contact with excess salt overnight. Integration of the  $^1\text{H}$  nmr spectra of the saturated solutions indicated a solubility of less than 0.004 M for each solution. This solubility is considerably less

than that required (0.17 M) to account for the peak at 118 Hz in pyridine-borane/pyridine-iodoborane solutions similar to that illustrated in Figure 53. In an attempt to identify the species absorbing at 118 Hz, cyclohexane was added to a solution of 1.0 M each in 4-methylpyridine-iodoborane and 4-methylpyridine-borane after 18 hr of reaction at room temperature in a glove bag. Before the addition of cyclohexane no precipitate was present, and the  $^1\text{H}$  nmr spectrum of the solution contained the peak at 118 Hz. After the addition of cyclohexane a white precipitate formed and the peak at 118 Hz in the nmr spectrum of the solution had diminished in relative area. The infrared spectrum of the precipitate was identical to that of an analyzed sample of bis(4-methylpyridine)boronium iodide. The identification of the extraneous  $^1\text{H}$  nmr peak as attributable to supersaturated boronium iodide was supported by the observation that precipitation was facilitated by seeding of the reaction mixture with finely ground glass or boronium iodide, or by striking the reaction vessel. Likewise, the new species visible in a freshly prepared solution of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in methylene chloride was identified as the boronium iodide by the observed enhancement of the absorptions in question upon the addition of a quantity of bis(4-methylpyridine)boronium iodide.

Reaction of Diborane with Bis(4-methylpyridine)boronium Iodide

Pure, dry bis(4-methylpyridine)boronium iodide (1.00 g,

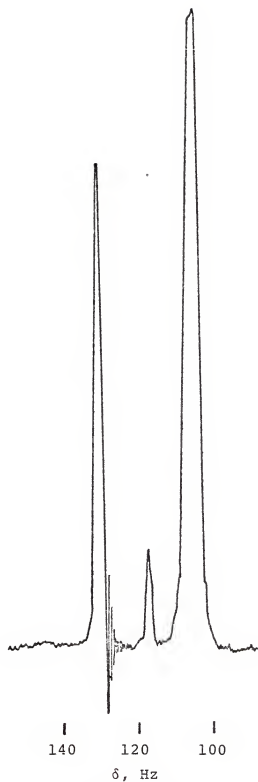


Figure 53.  $^1\text{H}$  nmr spectrum of a benzene solution of 4-methylpyridine-borane and 4-methylpyridine-iodoborane after 1 hr at room temperature;  $[4\text{-CH}_3\text{pyBH}_3] = [4\text{-CH}_3\text{pyBH}_2\text{I}] = 0.500$ . The solution also contained 0.0984 M mesitylene ( $\delta = 130$  Hz).

3.07 mmole) was placed in a 3-neck 100 ml flask connected to an nmr tube with one vacuum adapter and to the vacuum line with another. The flask was evacuated, and 3.2 ml of methylene chloride and 2.49 mmole of freshly purified diborane were condensed onto the boronium iodide. This quantity of diborane was sufficient to give a partial pressure of the gas of approximately 300 mm if none of it dissolved. The mixture was warmed to room temperature and stirred for 64 hr. Next the flask was tilted to transfer a portion of the reaction mixture to the attached nmr tube which was then sealed. Integration of the  $^1\text{H}$  nmr spectrum of the solution revealed that only 2.5% of the boronium iodide had reacted. The appearance of the product peaks suggested the formation of 4-methylpyridine-borane and 4-methylpyridine-iodoborane. The former compound was identified by the quantitative addition of 4-methylpyridine-borane directly to an nmr sample of the reaction mixture. The peaks attributed to 4-methylpyridine-borane increased in size by the expected amount and no new peaks were visible. Further reaction of the sealed tube sample for 6 more days at an estimated pressure of diborane of 22 atm resulted in the total consumption of 6.0% of the boronium cation. The appearance of a sharp singlet at 396 Hz suggested that some solvolysis had occurred.

In an identical experiment, the volatile materials were removed from the reaction flask after 38 hr of reaction, the residue was dissolved in 15 ml of water, and the unreacted

boronium iodide was converted to the hexafluorophosphate salt.<sup>52</sup> The  $^1\text{H}$  nmr spectrum of the salt was identical to that of authentic bis(4-methylpyridine)boronium hexafluorophosphate with no detectable impurities (m p = 129.0-129.5, lit. 132.5-133).<sup>50</sup> The quantity of the boronium hexafluorophosphate isolated (0.984 g, 286  $\mu\text{mole}$ ) corresponded to a 93.2% recovery of unreacted boron cation.

Reaction of 4-Chloropyridine-Iodoborane with Tetra(n-butylammonium Borohydride)

The tetra(n-butyl)ammonium borohydride used was in a mixture with tetra(n-butyl)ammonium iodide that contained 28% of the borohydride salt by weight.<sup>56</sup> Solid tetra(n-butyl)ammonium borohydride/iodide mixture (0.46 g, 9.5  $\mu\text{mole}$  of borohydride) was added to 1.0 ml of a 0.50 M solution of 4-chloropyridine-iodoborane in methylene chloride. As the borohydride salt was added, a gas that darkened silver nitrate paper was vigorously evolved. After 15 min of reaction at room temperature, the  $^1\text{H}$  nmr spectrum of the solution indicated that 92.% of the amine-iodoborane had reacted. After 10 min more, the amine-iodoborane resonances had disappeared from the spectrum completely. The only absorbing product was identified as 4-chloropyridine-borane by the quantitative addition of a portion of this compound directly to the nmr sample of the reaction mixture. The resonances assigned to 4-chloropyridine-borane increased in intensity by the expected amount, and no new peaks were visible.

Ultraviolet Spectra of Substituted Pyridine-Boranes and Pyridine-Iodoboranes

Ultraviolet spectra were obtained for some substituted pyridine-boranes and their monoiodinated derivatives in methylene chloride from 350-230 nm for 4-methyl, 4-chloro, and 2,6-dimethyl substitution. Iodoborane solutions were prepared by mixing appropriate aliquots of stock solutions of the corresponding amine-borane and iodine. A slight excess (3-5%) of the pyridine-borane was used to avoid spectral complications due to unreacted iodine or triiodide ion. Precautions necessary to prevent exposure of the sample solutions to light and air were taken, and spectra were obtained on freshly prepared samples. The spectra are summarized in Table 18. In each case, the shoulders observed in the amine-borane spectrum were broadened in the corresponding amine-iodoborane spectrum, and absorption was generally more intense throughout the spectrum of the iodinated derivative. In addition, for 4-methyl and 4-chloro substitution, a broad medium absorption appeared as a shoulder on the red side of the main absorption in the amine-iodoborane spectrum. No such absorption was present in the amine-borane spectra. A comparison of the spectrum of a pyridine-borane and its iodinated derivative is provided in Figure 54 for the 4-chloro-derivative. A similar shoulder was not readily visible for the 2,6-dimethyl derivative, but a comparison of the amine-borane and amine-iodoborane spectra suggests its presence.

Ultraviolet spectra of 4-methylpyridine-borane and 4-

Table 18  
Ultraviolet Spectral Data for Substituted  
Pyridine-Boranes and Pyridine-Iodoboranes

R in R-py	Solvent	R-pyBH <sub>3</sub>		R-pyBH <sub>2</sub> I	
		$\lambda_{\text{max}}(\text{nm})$	$E_{\text{max}} \times 10^{-3}$	$\lambda_{\text{max}}(\text{nm})$	$E_{\text{max}} \times 10^{-3}$
4-CH <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	232	6.34	<230	12.
		254 <sup>a</sup>	4.23	270	3.7
		262	3.61	285 <sup>b</sup>	2.2
		268	2.29		
	Cl <sub>4</sub>	<250	>5.2	<260	>7.5
		264 <sup>a</sup>	4.03	300 <sup>b</sup>	2.32
		270 <sup>a</sup>	2.85		
	cyclohexane	217	5.99	<210	>12.
		223	4.98	242	8.58
		251	5.39	305 <sup>b</sup>	1.81
		263 <sup>a</sup>	4.60		
4-Cl	CH <sub>2</sub> Cl <sub>2</sub>	243	7.32	239	11.5
		260 <sup>a</sup>	5.53	256 <sup>a</sup>	6.3
		267 <sup>a</sup>	4.37	262 <sup>a</sup>	5.15
		275 <sup>a</sup>	2.60	292 <sup>b</sup>	1.65
2,6-(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	238	3.49	237	7.01
		272 <sup>a</sup>	5.02	280	7.75
		276	8.26		
		284	4.48		

<sup>a</sup> Small shoulder

<sup>b</sup> Broad shoulder assigned as a charge transfer transition



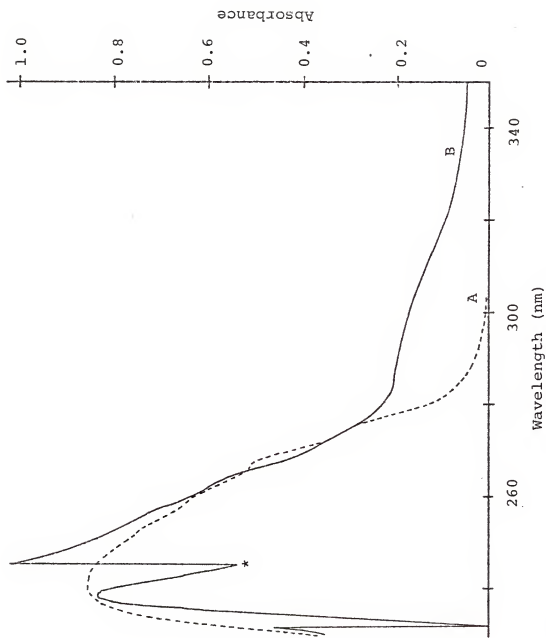


Figure 54. Ultraviolet spectra of 4-chloropyridine adducts in methylene chloride. Spectrum A corresponds to  $1.20 \times 10^{-4}$  M 4-ClpyBH<sub>3</sub> and spectrum B to  $1.16 \times 10^{-4}$  M 4-ClpyBH<sub>2</sub>I. Path length = 1 cm. \*Add 0.500 to absorbance.

methylpyridine-iodoborane were also obtained in carbon tetrachloride (350-250 nm) and cyclohexane (350-210 nm). The results are summarized in Table 18. The spectra of the amine-iodoborane in these solvents have the same general appearance as the spectrum of the methylene chloride solution. The broad absorption on the red side of the main peak is also visible in these solvents, although it is shifted to longer wavelength than in methylene chloride. Figure 55 provides a comparison of the 4-methylpyridine-iodoborane spectra in methylene chloride and cyclohexane.

Verification of the authenticity of the 4-methylpyridine-iodoborane spectrum

The absorptions attributed to the solute in the ultraviolet spectrum of 4-methylpyridine-iodoborane in cyclohexane were verified as authentic by the conversion of the amine-iodoborane to the bis(4-methylpyridine)boronium iodide by the addition of 4-methylpyridine. To 156 ml of  $9.57 \times 10^{-4}$  M 4-methylpyridine-iodoborane in cyclohexane were added 4.80 ml of  $3.41 \times 10^{-2}$  M 4-methylpyridine in cyclohexane (10% excess). The white precipitate which formed was isolated by filtration, washed with solvent, and dried under vacuum to give  $0.0482 \pm 0.0005$  g (99.2 $\pm$ 1.0% yield) of pure bis(4-methylpyridine)boronium iodide. The infrared and  $^1\text{H}$  nmr spectra ( $\text{CH}_2\text{Cl}_2$ ) of the product were identical to those of an analyzed sample of the boronium iodide. The ultraviolet spectrum of the filtrate from the isolation of the salt indicated complete loss of the absorptions attributed to the amine-iodoborane including the

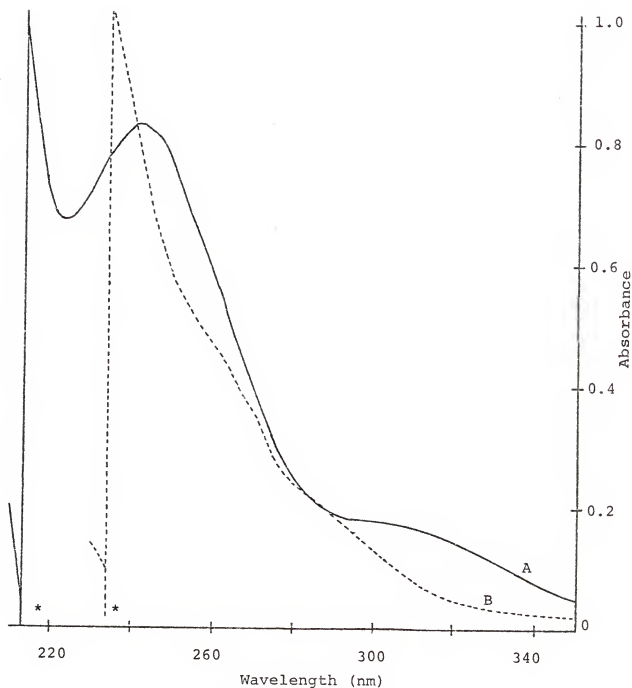


Figure 55. Ultraviolet spectra of 4-methylpyridine-iodoborane. Spectrum A corresponds to a  $9.70 \times 10^{-4}$  M solution in cyclohexane and spectrum B to a  $9.63 \times 10^{-4}$  solution in methylene chloride. Path length = 1 mm. \*Add 0.500 to absorbance

broad shoulder at 305 nm. The observed spectrum was exactly that expected for complete conversion of the amine-iodoborane to the boronium salt.

In a similar experiment in methylene chloride, the ultraviolet spectrum of the solution resulting from the addition of excess (11%) 4-methylpyridine to a solution of 4-methylpyridine-iodoborane was identical to that of an authentic sample of bis(4-methylpyridine)boronium iodide:  $\lambda_{\text{max}} < 233 \text{ nm}$ ,  $E_{\text{max}} > 2.4 \times 10^4$ ;  $\lambda_{\text{max}} = 246 \text{ nm}$ ,  $E_{\text{max}} = 1.88 \times 10^4$ ;  $\lambda_{\text{max}} = 263 \text{ nm (wk, sh)}$ ,  $E_{\text{max}} = 7.7 \times 10^3$ ; and  $\lambda_{\text{max}} = 325 \text{ nm}$ ,  $E_{\text{max}} = 9.0 \times 10^2$ . The broad absorption at 287 nm was completely removed by the addition of 4-methylpyridine.

## CHAPTER IV DISCUSSION

### Identification of Products and Interpretation of NMR Spectra

When methylene chloride solutions of a substituted pyridine-borane ( $R\text{-pyBH}_3$ ) and trimethylamine-iodoborane ( $(\text{CH}_3)_3\text{NBH}_2\text{I}$ ) were mixed at or near room temperature, the  $^1\text{H}$  nmr spectrum of the resulting freshly prepared mixture was not as expected for simple additivity of the solute spectra. For 4-methyl substitution, the aliphatic region of the spectrum was expected to exhibit a singlet at 148 Hz for the methyl resonance of 4-methylpyridine-borane, and a singlet at 169 Hz for trimethylamine-iodoborane. Instead, a more complicated spectrum was observed with an additional singlet at 156 Hz. On further standing, the peak at 156 Hz increased in relative intensity, the trimethylamine-iodoborane resonance decreased, and the peak attributed to the 4-methylpyridine aliphatic resonance shifted slightly downfield. After 4-5 hr at 35°C the basic features of the spectrum became stable, and a spectrum similar to that presented in Figure 56 resulted. The aromatic region of the spectrum was also more complicated than the simple spectrum anticipated for 4-methylpyridine-borane. Neither of the doublets ( $\delta=438$  Hz and 503 Hz;  $J=6$  Hz) expected for 4-methyl-

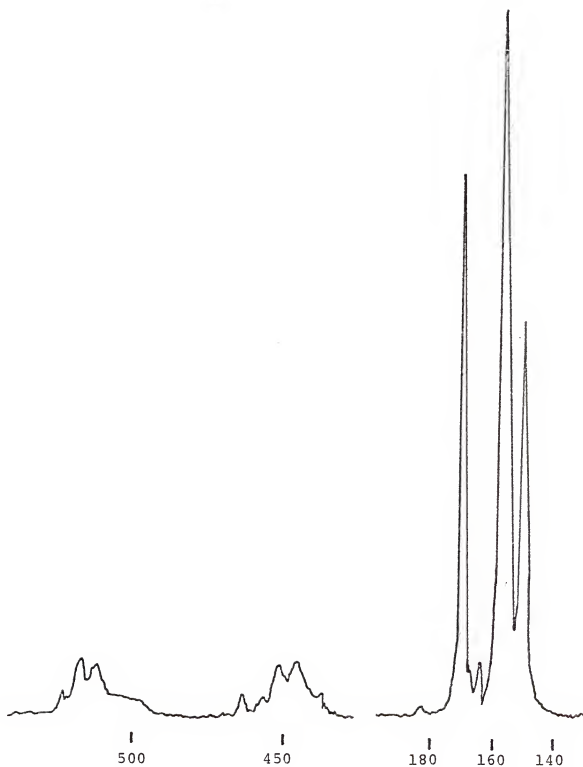
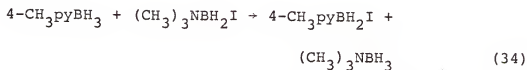


Figure 56.  $^1\text{H}$  nmr spectrum of the reaction mixture from 4-methylpyridine-borane and trimethylamine-iodoborane after 5 hr at  $35^\circ\text{C}$  in methylene chloride;  $[4\text{-CH}_3\text{pyBH}_3]_0 = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 = 0.50$ .

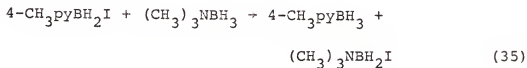
pyridine-borane was observed, but only broad resonances with no fine structure appeared at these chemical shifts. In addition, two doublets were seen further downfield at 448 and 516 Hz.

The position and shape of the peak at 156 Hz were consistent with its assignment as a resonance of trimethylamine-borane  $((\text{CH}_3)_3\text{NBH}_3)$ , which exhibited an identical absorption at comparable concentrations in methylene chloride. Further, the resonances attributed to the 4-methylpyridine moiety in Figure 56 were similar to those observed (vide infra) for a mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in the same solvent. Consequently, it is reasonable to postulate that 4-methylpyridine-borane and trimethylamine-iodoborane react in methylene chloride solution to produce 4-methylpyridine-iodoborane and trimethylamine-borane.

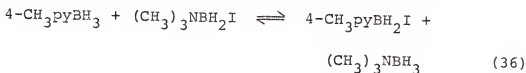


Secondly, it appears that the reaction comes to equilibrium, since the rate of trimethylamine-borane formation was rapid at first, then declined, and finally came to an apparent halt after 4-5 hr.

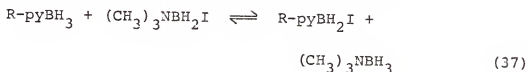
Both of these hypotheses were tested by attempting the reverse reaction.



If the products of reaction 34 have indeed been correctly identified, and the reaction does in fact reach equilibrium, then a mixture of 0.50 M 4-methylpyridine-iodoborane and 0.50 M trimethylamine-borane should exhibit an  $^1\text{H}$  nmr spectrum in methylene chloride identical to Figure 56 after 4-5 hr reaction time. The spectrum of such a solution was in fact identical to Figure 56, so that the formulation of a reversible hydrogen-iodine redistribution reaction between two 4-coordinate boron atoms appears to be valid.



Under comparable conditions, solutions of trimethylamine-iodoborane and the borane adducts of other pyridine derivatives exhibited similar behavior in the  $^1\text{H}$  nmr spectra. In each case, resonances attributed to the presence of trimethylamine-borane and the corresponding pyridine-iodoborane were observed. Further, the rate of appearance of the trimethylamine-borane peak gradually declined and finally stopped after 4-5 hr at 35°C. Thus, it is evident that the reversible hydrogen-iodine exchange reaction observed for 4-methylpyridine-borane can be generalized to other pyridine-boranes with  $\text{R}=\text{H}$ , 4-Cl, 2- $\text{CH}_3$ , 2,6- $(\text{CH}_3)_2$ , and 2- $\text{C}(\text{CH}_3)_3$  as well as 4- $\text{CH}_3$  in reaction 37.





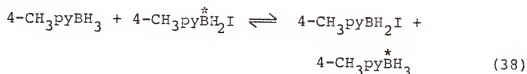
Although the  $^1\text{H}$  nmr resonances of the trimethylamine-containing species in Figure 56 are those expected for a mixture of the amine-borane and the amine-iodoborane, a similar statement cannot be made for the 4-methylpyridine absorptions. A spectrum of a simple mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane should exhibit two partially resolved singlets at 148 and 151 Hz in the aliphatic region. Instead, only one methyl signal with an intermediate chemical shift (150 Hz) is observed for the two solutes. Likewise, the aromatic region of the spectrum in Figure 56 does not indicate simple additivity of the solute spectra. The downfield portion of the aromatic spectrum should contain two completely resolved doublets for the 2,6-ring proton resonances of 4-methylpyridine-borane ( $\delta=503$  Hz,  $J=6$  Hz) and 4-methylpyridine-iodoborane ( $\delta=518$  Hz,  $J=7$  Hz). Instead, the amine-iodoborane doublet is shifted slightly upfield ( $\delta=516$  Hz) and is partially collapsed ( $J=5$  Hz), and the amine-borane resonance has completely collapsed to a broad absorption with no fine structure. A third unidentified resonance can be seen further downfield at 523 Hz. Similar observations can be made for the upfield aromatic resonances corresponding to the 3,5-ring protons. The pyridine-borane doublet expected at 438 Hz ( $J=6\frac{1}{2}$ ) has collapsed, the pyridine-iodoborane doublet expected at 447 Hz ( $J=7$  Hz) is partially collapsed ( $J=6$  Hz) and is shifted downfield ( $\delta=449$  Hz), and a third unidentified resonance

appears as a doublet at 461 Hz ( $J=7$  Hz).

The behavior described above for the 4-methylpyridine resonances in the  $^1\text{H}$  nmr spectrum of the reaction mixture of 4-methylpyridine-borane and trimethylamine-iodoborane is typical of a fresh mixture containing 4-methylpyridine-borane and 4-methylpyridine-iodoborane. Figures 44-C and 49-A illustrate this point for a freshly prepared solution with 0.50 M concentrations each of the pyridine-borane and pyridine-iodoborane. In the downfield region of the aromatic spectrum, both of the doublets expected for the solutes have collapsed and are partially merged to one broad absorption from 490-530 Hz. Superimposed on this broad absorption is a small doublet at 523 Hz ( $J=7$  Hz). Likewise, the upfield portion of the aromatic spectrum has none of the fine structure expected for the absorptions of the 3,5-ring protons of the pyridine-borane and pyridine-iodoborane. Instead, a broad absorption from 430-455 Hz and a small doublet at 462 Hz ( $J=7$ ) are observed. The aliphatic portion of the  $^1\text{H}$  nmr spectrum of the same solution (Figure 49-A) does not consist of the two singlets of equal areas expected at 148 and 151 Hz for the methyl resonances of the solutes. The observed spectrum consists of a slightly broadened singlet of an intermediate chemical shift ( $\delta=149\ 1/2$  Hz), and a much smaller singlet at 154 Hz.

The broadening of the aromatic resonances, and the merging of the methyl resonances in this spectrum are typical phenomena for species involved in chemical exchange.<sup>57</sup>

In light of the existence of the exchange reaction observed between 4-methylpyridine-borane and trimethylamine-iodoborane (reaction 36), and the expected similarity in the reactivities of pyridine-iodoboranes and trimethylamine-iodoborane toward nucleophiles, it is quite reasonable to postulate that intermolecular hydrogen-iodine exchange occurs between 4-methylpyridine-borane and 4-methylpyridine-iodoborane.



Sufficiently rapid exchange on the nmr time scale would cause a loss of the individual identities of the two types of 4-methylpyridine rings in the system. In the presence of rapid exchange the aliphatic region of the spectrum would consist of one singlet with a chemical shift halfway between the positions of the signals for the two exchanging solutes when they are present in equal molar concentrations. This type of spectrum is observed in Figure 49-A ( $\delta=149\ 1/2$  Hz), although the slight broadening of the singlet relative to the widths of the individual solute methyl resonances suggests that the exchange process is not quite rapid enough to cause a complete merger of the two signals.

This analysis predicts that the aromatic resonances for the two types of pyridine rings should be further from complete merger, since the differences in chemical shifts ( $\Delta\delta$ ) are larger than for the aliphatic resonances. In the absence

of exchange, the methyl absorptions of the individual solutes are separated by 3 Hz, while for the aromatic resonances  $\Delta\delta=15$  Hz and  $\Delta\delta=9$  Hz, respectively, for the 2,6- and 3,5-ring proton peaks. The above prediction is confirmed by the appearance of the spectrum presented in Figure 44-C. The two doublets for the 2,6-aromatic resonances are partially merged. Complete merger would produce one doublet at 510 Hz with a peak width at half height of approximately 9 Hz. The observed resonance is a broad absorption from 490-530 Hz with a peak width at half height of about 22 Hz with none of the fine structure of a doublet. Similar observations can be made for the 3,5-ring proton resonances. Consequently, the spectra are consistent with intermolecular hydrogen-iodine exchange (reaction 33) with lifetimes of the participating species roughly equal to the frequency separations ( $\Delta\delta$ ) of their  $^1\text{H}$  nmr signals.

There are certain differences in the features of the 4-methylpyridine resonances in Figure 56 compared to Figures 49-A and 44-C that are consistent with the preceding analysis. Figure 44-C presents the spectrum of a solution with equal concentrations of each solute, whereas the solution corresponding to Figure 56 contained a concentration of 4-methylpyridine-iodoborane that was more than double that of 4-methylpyridine-iodoborane (cf Table 1). The aliphatic resonance in Figure 56 is slightly closer to the chemical shift of 4-methylpyridine-iodoborane than the corresponding absorption in Figure 49-A. This difference is expected since the

chemical shift of the merged peak should be halfway between the chemical shifts of the two exchanging solutes if their concentrations are equal, and closer to the position of the more abundant solute if the concentrations are unequal. Likewise, the aromatic resonances in Figure 56 are more characteristic of 4-methylpyridine-iodoborane than those in Figure 44-C.

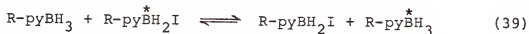
The appearance of the  $^{11}\text{B}$  nmr spectrum of an equimolar mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in methylene chloride (Figure 52-C) is also consistent with intermolecular hydrogen-iodine exchange (reaction 38). The chemical shifts of the two separate solutes are nearly identical, so that the individual resonances are expected to coincide even in the absence of chemical exchange. However, in the absence of exchange, spin coupling of hydrogen to boron should be retained so that the spectrum of the non-reacting mixture should exhibit some fine structure due to spin-spin interactions. The observed spectrum consists of a singlet with no fine structure, supporting the preceding interpretation of chemical exchange between the two solutes.

More conclusive evidence for the existence of facile hydrogen-iodine exchange between molecules of 4-methylpyridine-borane and 4-methylpyridine-iodoborane is provided by the temperature dependence of the  $^1\text{H}$  nmr spectrum of a mixture of these solutes. If the loss of resolution and partial merger of the resonances in Figures 44-C and 49-A are in fact due to a chemical exchange process, then adequate

suppression of the reaction rate should produce the spectra expected for each of the solutes in the absence of exchange. Sufficient deceleration of the exchange process might be accomplished by lowering the temperature of the reaction mixture. Low temperature  $^1\text{H}$  nmr spectra of an equimolar mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in 1,1,2,2-tetrachloroethane are presented in Figure 50. As temperature decreases, the broad absorption of the 2,6-aromatic protons displays some fine structure, and the presence of two doublets becomes progressively more apparent. Finally, at  $-45^\circ\text{C}$ , two doublets with the chemical shifts and coupling constants expected for the solutes in the absence of exchange are resolved. A similar transformation is evident for the 3,5-aromatic resonances, but partial overlap of the resolved doublets occurs due to a smaller value of  $\Delta\delta$ . The effects of cooling on the aliphatic region of the spectrum can be seen in Figure 51. As temperature decreases, the methyl singlet broadens, until at  $-48^\circ\text{C}$  the individual resonances of 4-methylpyridine-borane and 4-methylpyridine-iodoborane are partially resolved. The attainment of spectra at even lower temperatures was not possible, but the nature of the spectra suggests that exchange was still occurring at  $-48^\circ\text{C}$ , since the resolution of the two methyl peaks in the mixture did not quite correspond to the chemical shift difference of 3 Hz measured in solutions of the separate pure components. Complete resolution of the 2,6-aromatic peaks

( $\Delta\delta = 15$  Hz) required cooling to  $-45^\circ\text{C}$ , and considerably lower temperatures should be necessary for maximum resolution of the methyl signals ( $\Delta\delta = 3$  Hz).

The hydrogen-iodine exchange reaction that occurs in a solution of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in methylene chloride was observed for other pyridine derivatives as well.



The  $^1\text{H}$  nmr spectra of equimolar mixtures of  $\text{R-pyBH}_3$  and  $\text{R-pyBH}_2\text{I}$  in methylene chloride for  $\text{R}=\text{H}$ , 4-Cl, 2- $\text{CH}_3$ , and 2,6- $(\text{CH}_3)_2$  (Figures 45-48), all have the same general features as described previously for the 4-methyl derivative. In the aromatic region, the spectra all display broadening, loss of resolution, and mergence or partial mergence of the pyridine-borane and pyridine-iodoborane resonances. Further, the aliphatic signals of the methyl-pyridine derivatives are merged to one slightly broadened peak for 2,6-dimethyl substitution, and are partially merged for 2-methyl substitution (Figures 49-B and 49-C and Table 17).

One other feature of the  $^1\text{H}$  nmr spectra of the pyridine-borane/pyridine-iodoborane solutions is noteworthy. For each derivative, the aromatic and/or aliphatic region of the spectrum of the freshly prepared mixture contains one or more low-intensity resonances not assigned to either of the initial solutes. Further, these peaks appeared rapidly at first, and then the rate of their production de-

creased dramatically.\* For example, for the 4-chloropyridine derivative, the initial spectrum of the mixture contained two small doublets ( $J=7$  Hz) at 473 and 545 Hz (Figure 48-C). These peaks were identified unequivocally as resonances due to the formation of  $(4\text{-Clpy})_2\text{BH}_2^+$ , the bis(4-chloropyridine)boronium cation, most of which precipitated from the reaction mixture as the slightly soluble iodide salt. After conversion of the compound from the iodide to the hexafluorophosphate salt, examination of its solubility and spectral ( $^1\text{H}$  nmr and infrared) properties established its identity as bis(4-chloropyridine)boronium hexafluorophosphate,  $(4\text{-Clpy})_2\text{BH}_2^+\text{PF}_6^-$ . The properties of the salt were identical to those of an analyzed sample of  $(4\text{-Clpy})_2\text{BH}_2^+\text{PF}_6^-$  prepared by the well-documented procedure of Ryschkewitsch,<sup>49,50</sup> wherein the cation was produced by the displacement of iodide ion from 4-chloropyridine-iodoborane by 4-chloropyridine. These results, and those presented elsewhere (vide infra), verified the formation of the bis(4-chloropyridine)boronium cation in mixtures of 4-chloropyridine-borane and 4-chloropyridine-iodoborane, and permitted the assignment of the previously unidentified ab-

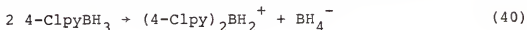
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\* A sudden decline in the rate of production of these peaks for 4-chloro substitution is not surprising due to the limited solubility of the bis(4-chloropyridine)boronium iodide salt. However, the formation of a saturated solution cannot account for similar phenomena observed for the other derivatives, since the corresponding boronium iodides are quite soluble in methylene chloride.

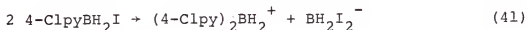


sorptions in the  $^1\text{H}$  nmr spectra of such mixtures as resonances of the boronium cation.

The bis(4-chloropyridine)boronium cation could conceivably be formed from the disproportionation of either of the solutes present in the mixture in a reaction analogous to the donor-ligand exchange generalized by equation 10.

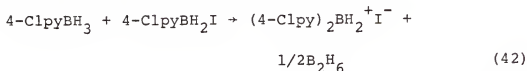


or



However, solutions containing only one of these compounds in methylene chloride failed to react under conditions which led to extensive boronium cation formation for a mixture of both solutes. Thus, it is evident that both species are required for boron cation formation.

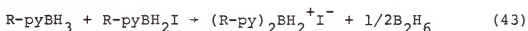
The stoichiometry of the reaction was established by the reaction of 4-chloropyridine-borane and 4-chloropyridine-iodoborane in benzene in a vacuum system. An 89.2% yield of the iodide salt of the bis(4-chloropyridine)boronium cation, and a 76.2% yield of pure diborane were isolated for the reaction mixture based on equation 42.



The products were identified unequivocally by comparison of their spectral and physical properties with those of authentic samples, and, in the case of the boronium cation, by elemental analysis of the hexafluorophosphate derivative.

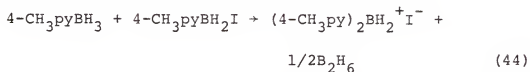
The discrepancy in the yields of diborane and the boronium iodide was attributed to the observed leakage of the trap portion of the vacuum manifold on long standing. No other volatile boron hydrides were formed, in agreement with equation 42. The weight of nonvolatile residue from the reaction mixture was within 2% of the amount expected for the unreacted starting materials.

It is expected that the unidentified absorptions in the  $^1\text{H}$  nmr spectra of the other substituted pyridine-borane/pyridine-iodoborane mixtures (Figures 45 - 49) are likewise attributable to the formation of the corresponding bis(pyridine)boronium cations (reaction 43), and further, that the iodide salts of the cations might be prepared in a manner analogous to that used to synthesize the bis(4-chloropyridine)-boronium iodide.



The validity of both of these postulates has been demonstrated for the 4-methylpyridine derivative. When solid bis(4-methylpyridine)boronium iodide was added to a solution of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in methylene chloride, the peaks attributed to the boronium iodide in Figures 44 and 49-A increased in intensity by the calculated amount, and no new absorbances were detectable. Thus, the assignment of these resonances as absorptions of the bis(4-methylpyridine)boronium cation is reasonable. Further, an 87% yield of pure bis(4-methylpyridine)boronium iodide was

isolated from the reaction of 4-methylpyridine-borane and 4-methylpyridine-iodoborane in refluxing benzene.

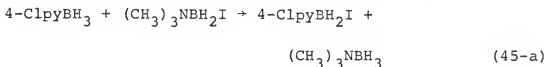


The evolved diborane was identified qualitatively by the reaction of the effluent gas from the reaction mixture with 4-methylpyridine to form 4-methylpyridine-borane.

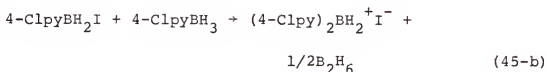
The foregoing establishment of the existence of reactions 39 and 43 was prerequisite to the rational interpretation of the  $^1\text{H}$  nmr spectra of the solutions that result upon mixing a pyridine-borane and trimethylamine-iodoborane in methylene chloride (cf e.g. Figure 56). In such mixtures, hydrogen-iodine exchange between pyridine and trimethylamine adducts results in the formation of the pyridine-iodoborane which is then available for hydrogen-iodine exchange with unreacted pyridine-borane (reaction 39) and for boronium cation formation, again by reaction with the pyridine-borane (reaction 43). The former reaction accounts for the broadness, loss of resolution, and merger of the pyridine resonances generally observed in the mixtures, and the latter reaction accounts for the minor extraneous resonances that gradually increased in intensity.

Further evidence that a pyridine-borane exchanges hydrogen for iodine with trimethylamine-iodoborane was provided by the isolation of the bis(4-chloropyridine)boronium iodide salt from a mixture of 4-chloropyridine-borane and trimethyl-

amine-iodoborane. As mentioned previously, a solution of 4-chloropyridine-borane alone does not produce the boronium iodide, but the reaction of a mixture of the pyridine-borane and the pyridine-iodoborane does form the boron cation (reaction 42). Thus, it is evident that iodination of 4-chloropyridine-borane occurs in the presence of trimethylamine-iodoborane, and the following reaction sequence to account for boronium iodide formation is quite reasonable.



then



Consequently, when a pyridine-borane is mixed in solution with trimethylamine-iodoborane, or when trimethylamine-borane is mixed in solution with a pyridine-iodoborane, three reactions occur simultaneously (reactions 37, 39, and 43). Each of these reactions must be considered in the interpretation of the  $^1\text{H}$  nmr spectra of the resulting mixtures.

#### Hydrogen-Halogen Exchange Reactions

##### Hydrogen-Iodine Exchange Equilibria and Thermochemical Considerations

Reaction 37 represents the first reported exchange of substituents on boron between complexes of different donor molecules. As such, it provides a system in which the

effects of altering the properties of one donor molecule can be investigated while keeping the other donor constant. The presence of the pyridine ring in the borane adducts affords the opportunity to independently examine the steric and electronic effects on the exchange equilibrium by the use of a variety of substituted pyridine derivatives. Equilibrium constants ( $K_{eq}$ ) were determined for reaction 37 in methylene chloride at 35°C for R=H, 4-CH<sub>3</sub>, 4-Cl, 2-CH<sub>3</sub>, 2,6-(CH<sub>3</sub>)<sub>2</sub>, and 2-C(CH<sub>3</sub>)<sub>3</sub> by the integration of <sup>1</sup>H nmr spectra of equilibrium mixtures (cf Table 1).

$$K_{eq} = \frac{[R-pyBH_2I]_e [(CH_3)_3NBH_3]_e}{[R-pyBH_3]_e [(CH_3)_3NBH_2I]_e} \quad (46)$$

In each case, equilibrium with respect to hydrogen-iodine exchange was attained in 3 to 5 hr for approximately one molar concentration of each reagent. Nevertheless, the <sup>1</sup>H nmr spectra of the solutions changed gradually in appearance on longer standing because of variable extents of the reaction of the pyridine-borane and the pyridine-iodoborane to produce boronium iodide salt and diborane (reaction 43). For each system, the extent to which this side reaction had progressed during the attainment of hydrogen-iodine exchange equilibrium was taken into account when calculating the value of the equilibrium constant.

Side reaction 43 caused shifts in the positions of the hydrogen-iodine exchange equilibria as indicated by a gradual decrease in the ratio  $[(CH_3)_3NBH_3]_e / [(CH_3)_3NBH_2I]_e$  for

each system. For each derivative, the initial concentrations of the reactants were equal, the initial concentrations of the products were zero and  $K_{eq} > 1$ , so that the ratio  $[R-pyBH_2I]_e/[R-pyBH_3]_e$  had to be greater than one. Any one-to-one net side reaction of the pyridine-borane and the pyridine-iodoborane (e.g. reaction 43) would then of necessity cause an increase in the ratio  $[R-pyBH_2I]_e/[R-pyBH_3]_e$ , and the ratio  $[(CH_3)_3NBH_3]_e/[(CH_3)_3NBH_2I]_e$  must decrease. The observed declines in the latter ratio were consistent with equilibrium expression 46, and with the equilibrium constants expressed in Table 1.

Table 19 lists equilibrium constants ( $K_{eq}'$ ) for hydrogen-iodine exchange between 4-chloropyridine-iodoborane and each of the unhindered pyridine-boranes.



Equilibrium constants for this reaction were calculated from the  $K_{eq}$  s for reaction 37 using  $K_{eq}'(R) = K_{eq}(R)/K_{eq}(4-Cl)$ .

Examination of Table 19 reveals that as the base strength of the pyridine moiety increases, the equilibrium constants ( $K_{eq}$  and  $K_{eq}'$ ) increase, for donors with comparable steric requirements in the vicinity of the boron-nitrogen bond. For the three derivatives with no ortho alkyl substituents, base strength and the equilibrium constants increase in the order  $R=4-Cl < H < 4-CH_3$ . In reaction 47, equilibrium is favored with the stronger base coordinated to iodoborane, and the weaker base coordinated to borane.

Table 19  
Equilibrium Constants for  
Hydrogen-Iodine Exchange

R	$pK_a$ of R-pyH <sup>+</sup>	$K_{eq}^a$	$K_{eq}^{1a}$	$K_{eq}^{2a}$
4-Cl	3.83 <sup>b</sup>	1.29	1.00	
H	5.17 <sup>c</sup>	2.18	1.69	
4-CH <sub>3</sub>	6.02 <sup>c</sup>	3.96	3.07	1.00
2-CH <sub>3</sub>	5.97 <sup>c</sup>	1.78		0.450
2,6-(CH <sub>3</sub> ) <sub>2</sub>	6.75 <sup>c</sup>	3.56		0.899
2-C(CH <sub>3</sub> ) <sub>3</sub>	5.76 <sup>c</sup>	1.89		0.477

<sup>a</sup> In methylene chloride at 35°C

<sup>b</sup> Reference 58

<sup>c</sup> Reference 59

The relative acceptor strengths of  $BX_3$  Lewis acids toward amines have been established as decreasing in the series  $X=I>Br>Cl>H>F$  on the basis of mass spectral data, nmr chemical shifts, heats of formation of amine- $BX_3$  adducts, and dipole moment studies.<sup>60</sup> Interpolation of this trend to mixed acids suggests that  $BH_2I$  should be a stronger acceptor toward amines than  $BH_3$ . This notion is supported by a relationship established by Coyle and Stone correlating acceptor strength to infrared stretching frequencies for adducts containing boron-hydrogen bonds.<sup>61</sup> Myers has used this correlation to assign relative acid strengths to  $BH_3$ ,  $BH_2Cl$ , and  $BHX_2$  ( $X=Cl, Br, I$ ) toward trimethylamine.<sup>62</sup> A higher boron-hydrogen symmetric stretching frequency was indicative of a stronger boron-nitrogen dative bond, and consequently a stronger Lewis acid. In the present study, the positions of the infrared absorptions assigned to the symmetric boron-hydrogen stretching mode for solutions of 2,6-dimethylpyridine-borane ( $\nu_s=2270\text{ cm}^{-1}$ ) and 2,6-dimethylpyridine-iodoborane ( $\nu_s=2430\text{ cm}^{-1}$ ) in methylene chloride are consistent with a greater acceptor strength for  $BH_2I$  than  $BH_3$ .

As the base strength of the substituted pyridine increases, equilibrium 47 shifts toward  $R\text{-py}BH_2I$  in preference to  $R\text{-py}BH_3$ . The observed shifts suggest a greater sensitivity for the stronger acid ( $BH_2I$ ) to changes in the base strength of the donor (vide infra). That is, in the absence



of steric complications, an increase in the donor ability of the substituted pyridine favors its coordination to the stronger acid.

The results listed in Table 19 also reveal that the positions of the hydrogen-iodine exchange equilibria are affected by changes in the steric requirements of the pyridine molecule. As the ortho hydrogen atoms on the pyridine ring are replaced by methyl groups, the equilibrium constant ( $K_{eq}$ ) decreases for the first methyl substitution, and then increases for the next methyl substitution. In the absence of any steric effects, the equilibrium constant for 2-methyl substitution should be the same as that for 4-methyl substitution, considering the similarity in base strength of the two donors. Alternatively, the equilibrium constant for reaction 48 ( $K_{eq}$ ) for 2-methylpyridine-borane should be very close to one in the absence of any steric effects.



Table 19 lists values of  $K_{eq}$  for the ortho-substituted pyridine derivatives, where  $K_{eq}(R) = K_{eq}(R)/K_{eq}(4-CH_3)$ .

The discrepancies between the expected and observed values of the equilibrium constants for the 2-methylpyridine derivative are attributed to steric interactions of the ortho methyl group with the boron-substituents. The bulkier ortho group for 2-methylpyridine should be more sensitive to changes in the steric requirements of the boron substituents than the relatively small hydrogen atom at the same position

for 4-methylpyridine. Thus, substitution of iodine for hydrogen on boron should lead to a greater increase in steric interactions between the ortho pyridine substituents and the acid portion of the molecule for 2-methylpyridine than 4-methylpyridine. This steric factor should favor the left side of the exchange equilibria as written for the 2-methylpyridine system relative to 4-methylpyridine as a standard. The observed equilibrium constants are consistent with this analysis.

In the absence of steric effects, the equilibrium constants ( $K_{eq}$  and  $K_{eq}''$ ) for hydrogen-iodine exchange should be larger for 2,6-dimethylpyridine than for 4-methylpyridine, due to the greater basicity of the former amine. The observed equilibrium constants are actually greater for 4-methylpyridine. Again the discrepancies can be attributed to steric effects of the ortho methyl groups in the 2,6-dimethylpyridine system. However, the magnitude of the steric effects for the second methyl substitution is surprisingly small.

Likewise, the steric effects of the ortho t-butyl group are less than expected. The base strength of 2-t-butylpyridine is close to that of 2-methylpyridine, and the t-butyl group is considerably bulkier than the methyl group. Thus, an extrapolation of the steric effects observed for the 2-methyl system vs. the 4-methyl system suggests that the equilibrium constants ( $K_{eq}$  and  $K_{eq}''$ ) for 2-t-butylpyridine

should be significantly less than those for 2-methylpyridine. However, the observed equilibrium constants for these two derivatives are nearly identical.

Thus, it appears that as a donor 2-methylpyridine reveals a small difference in the steric requirements of  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  as acceptors, but that the bulkier 2,6-dimethylpyridine and 2-t-butylpyridine donors reveal no further difference. As an overview, the positions of the equilibria are fairly insensitive to alterations in the steric environment of the pyridine donor, suggesting that the steric requirements imposed by  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  toward pyridine donors are nearly identical.

An alternative, more quantitative analysis of the steric strains in these systems is provided by a thermochemical treatment of the equilibrium data. Reaction 37 is typical of a redistribution reaction in that the numbers and types of bonds remain constant. If constancy of bond enthalpy values could be assumed, such a reaction would be thermoneutral. Equilibrium in a thermoneutral reaction would be governed completely by entropy changes, and completely random distribution of groups would result. According to Van Wazer,<sup>5</sup> a system which undergoes random redistribution is one in which the exchange equilibria are entirely entropy controlled ( $\Delta H_{\text{random}} = 0$ ), and the only contribution to the entropy is that due to the rearrangement of the substituents ( $\Delta S_{\text{random}}$ ). Deviations from random behavior are attributable

to the enthalpy change and/or entropy contributions other than  $\Delta S_{\text{random}}$ . Van Wazer has demonstrated that in cases where the solvent molecules do not enter coordination spheres of the exchanging atoms, contributions to the entropy change other than the redistribution entropy itself can be ignored\*, so that

$$\Delta S \approx \Delta S_{\text{random}}$$

in which case deviations for randomness of the equilibrium can be attributed to enthalpy effects. A quantitative relationship between the enthalpy of the exchange reaction and the equilibrium constant can be derived as follows:

$$\Delta G_{\text{random}} = \Delta H_{\text{random}} - T\Delta S_{\text{random}}$$

or since  $\Delta H_{\text{random}} = 0$

$$\Delta G_{\text{random}} = -T\Delta S_{\text{random}}$$

For the observed equilibria,  $K_{\text{random}} = 1$ , and thus  $\Delta G_{\text{random}} = 0$  and  $\Delta S_{\text{random}} = 0$ .

Since  $\Delta S \approx \Delta S_{\text{random}}$ , then  $\Delta S = 0$ , and  $\Delta G = \Delta H$ . Thus,

$$\Delta H = -2.3RT \log K_{\text{eq}} \quad (49)$$

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\* Lappert has demonstrated the validity of this assumption for the exchange reactions of the boron trihalides in 1,1-dichloroethane.<sup>8</sup>

For each of the systems studied here,  $K_{\text{random}}$ , the equilibrium constant for a completely random distribution of hydrogen and iodine between the two complexes, is equal to one. For each derivative in reaction 37 the observed equilibrium constant was not unity, so that nonrandom exchange occurred.

The enthalpy of reaction 37 for each substituent was estimated from equation 49. The estimated enthalpies of reaction are listed in Table 20 as  $(\Delta H_1)_{\text{R-py}}$ . The tabulated error limits reflect the uncertainties in the values of  $K_{\text{eq}}$  (Table 1), but do not include any possible contributions introduced by the Van Wazer hypothesis ( $\Delta S \approx \Delta S_{\text{random}}$ ). The Van Wazer hypothesis was tested for 4-methyl substitution in reaction 37. Using the value of  $\Delta H_1$  obtained by assuming  $\Delta S \approx \Delta S_{\text{random}}$  (equation 49), the equilibrium constant expected at 0°C was calculated from  $\log \frac{K_{T_1}}{K_{T_2}} = \frac{\Delta H_1}{2.3R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$ , where  $T_1 = 308^\circ\text{K}$  and  $T_2 = 273^\circ\text{K}$ . The calculated value (4.80) of the equilibrium constant at 0°C was within the error limits of the observed value (Table 1), substantiating the validity of the Van Wazer assumption within experimental error.

The enthalpies of reaction for equation 37 were combined with some thermochemical data provided by Brown<sup>63</sup> in a thermodynamic cycle to obtain quantitative measurements of the steric strains in the ortho-substituted pyridine-iodoboranes. At the same time, the relative enthalpies for heterolytic boron-nitrogen bond cleavage (coordinate bond

Table 20  
Thermochemical Data

R	K <sup>a</sup> p <sup>a</sup>	( $\Delta H_1$ ) <sup>b</sup> R-py	$\Delta(\Delta H_1)_1^b$ R-py	( $\Delta H_2$ ) <sup>b,c</sup> R-py	$\Delta(\Delta H_2)_2^b$ R-py	$\Delta(\Delta H_5)_5^b$ R-py
4-Cl	3.83	-0.16 $\pm$ .03	0.32	16.90	-1.01	1.33
H	5.17	-0.48 $\pm$ .06	0	17.91	0	0
4-CH <sub>3</sub>	6.02	-0.84 $\pm$ .08	-0.36	18.45	+0.54	-0.90
2-CH <sub>3</sub>	5.97	-0.35 $\pm$ .04	0.13	17.16	-0.75	0.88
2,6-(CH <sub>3</sub> ) <sub>2</sub>	6.75	-0.77 $\pm$ .09	-0.29	16.34	-1.57	1.28
2-C(CH <sub>3</sub> ) <sub>3</sub>	5.76	-0.39 $\pm$ .06	0.09	12.11	-5.80	5.89

<sup>a</sup> See Table 19 for references

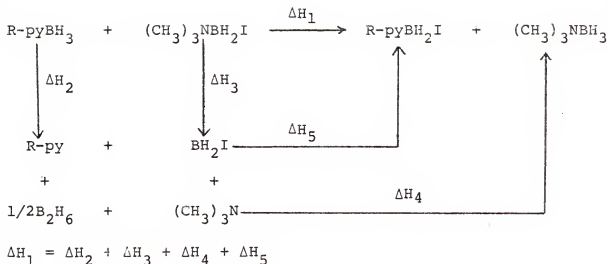
<sup>b</sup> Kcal/mole

<sup>c</sup> These enthalpies values were taken directly from Brown's data (reference 63) except for 4-chloropyridine-borane. For this derivative, ( $\Delta H_2$ )<sub>R-py</sub> was estimated by extrapolation of Brown's  $-\Delta(\Delta H_2)$ <sub>R-py</sub> vs.  $K_a$  plot to  $K_a = 3.83$ .

enthalpies) of the pyridine-iodoboranes investigated herein were determined, so that the electronic as well as steric effects on the boron-nitrogen coordinate bond enthalpies in these compounds could be examined.

Brown and coworkers have measured the heats of reaction of gaseous diborane with a number of pyridine derivatives.<sup>63,67</sup> For pyridine derivatives with hydrogen in both ortho positions there is a linear increase in the amount of heat evolved in the reaction with diborane as the base strength ( $K_a$  of the conjugate acid) of the amine increases. For pyridine derivatives with ortho alkyl substituents, the heats evolved on reaction with diborane were less than expected on the basis of base strength. The discrepancies were attributed to strains in the adducts due to the steric interactions between the ortho alkyl groups and the  $BH_3$  moiety. No analogous studies have been reported for the reactions of a series of donors with a haloborane ( $BH_2X$ ), presumably due to the inavailability of the free Lewis acid.

The enthalpy values calculated herein for reaction 37 ( $\Delta H_1$ ) and Brown's data for the heats of reaction of the corresponding pyridine derivatives with diborane ( $\Delta H_2$ ) were used to determine indirectly the relative heats of reaction of each donor with  $BH_2I$  as illustrated by the thermochemical cycle below. All steps refer to reactions in methylene chloride solution.



The heat of reaction of a pyridine donor with iodoborane,  $\Delta H_5$ , can be determined indirectly if the enthalpy changes of steps 1 through 4 are known. Values of  $\Delta H_1$  are provided herein for a number of pyridine donors. Brown's data for the heats of reaction of diborane with pyridine donors ( $-\Delta H_2$ ) supply measurements of  $\Delta H_2$ . A value of  $\Delta H_4$ , the heat of reaction of trimethylamine with diborane, can be inferred from enthalpy data for the dissociation of trimethylamine-borane into its Lewis acid and base fragments.<sup>64</sup> However, no data are available with respect to  $\Delta H_3$ , the coordinate bond enthalpy for trimethylamine-iodoborane. The absence of data for  $\Delta H_3$  precludes the possibility of calculating absolute values of  $\Delta H_5$ . Nevertheless, relative values of  $\Delta H_5$  can be determined for different pyridine donors, and therefore substituent effects on boron-nitrogen coordinate bond enthalpies in pyridine-iodoboranes can be examined. For this purpose, a quantity,  $\Delta(\Delta H_5)_{\text{R-py}}$ , is defined as the difference between the values of  $\Delta H_5$  for the substituted and unsubsti-



tuted pyridine donor.

$$(\Delta H_5)_{R-PY} = (\Delta H_5)_{R-PY} - (\Delta H_5)_{PY}$$

The values of  $\Delta H_3$  and  $\Delta H_4$  are independent of substitution on pyridine, and any variation in  $\Delta H_5$  can be attributed to variations in  $\Delta H_1$  and  $\Delta H_2$ . From the thermochemical cycle above

$$\Delta(\Delta H_5)_{R-PY} + \Delta(\Delta H_1)_{R-PY} - \Delta(\Delta H_2)_{R-PY} \quad (50)$$

where  $\Delta(\Delta H_1)_{R-PY}$  and  $\Delta(\Delta H_2)_{R-PY}$  represent the enthalpy differences between the substituted and unsubstituted pyridine donors for steps 1 and 2, respectively. Values of  $\Delta(\Delta H_1)_{R-PY}$  and  $\Delta(\Delta H_2)_{R-PY}$  for each of the pyridine derivatives under investigation are recorded in Table 20.

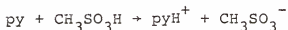
The differences in the solvents and temperatures used in Brown's work and in this study are not expected to be significant. Brown's enthalpy data refer to the reactions of gaseous diborane with the amine dissolved at 25°C in nitrobenzene to yield adduct in solution.



The ten degree temperature difference should have no significant effect on these reaction enthalpies. Step 2 in the above cycle refers to reaction to form diborane dissolved in methylene chloride, but any error introduced due to this difference from Brown's work makes a constant contribution to  $\Delta H_5$ , and consequently has no effect at all on  $\Delta(\Delta H_5)_{R-PY}$ . The only distinctions then between step 2 and reaction 51

are the relative solvation enthalpies of the pyridine and its borane adduct in methylene chloride vs. those in nitrobenzene. These differences can affect  $\Delta(\Delta H_5)_{R-py}$  only if they are sensitive to substitution on the pyridine.

Ryschkewitsch and Birnbaum<sup>65</sup> have concluded that the enthalpies of transferring a pyridine or its borane from nitrobenzene to 1-propanol are not likely to be sensitive to substitution on the pyridine, citing Brown's<sup>66</sup> observation that the relative enthalpies for the reaction



are completely unaffected by solvent changes. Thus, solvent effects on step 2 of the cycle are not expected to be significant.

Consequently, the heat of reaction of a substituted pyridine with  $BH_2I$  can be compared with that for pyridine itself simply by examining the differences in  $\Delta H_1$  and  $\Delta H_2$  for the two systems (equation 56). The resulting values of  $\Delta(\Delta H_5)_{R-py}$  for each derivative are presented in Table 20. The tabulated values of  $\Delta(\Delta H_5)_{R-py}$  allow an analysis of steric and electronic effects on the boron-nitrogen coordinate bond enthalpy in pyridine-iodoboranes. For the sterically similar derivatives ( $R=H$ ,  $4-CH_3$ , and  $4-Cl$ ), the amount of heat released on reaction with  $BH_2I$  increases as the base strength of the amine increases. Thus, in the absence of steric effects, the boron-nitrogen coordinate bond enthalpy in the pyridine-iodoborane adduct increases

as the base strength of the donor increases. Brown made similar observations for other Lewis acids ( $\text{BH}_3$ ,  $\text{BF}_3$ , and  $\text{B}(\text{CH}_3)_3$ ), and here, as in Brown's work, a linear relationship is observed between relative reaction enthalpies and  $pK_a$  as a measure of base strength in the absence of steric effects. Figure 57 is a plot of  $\Delta(\Delta H_5)_{\text{R-py}}$  for the unhindered pyridine donors. A linear relationship is observed with a negative slope. Alternatively, the boron-nitrogen coordinate bond enthalpy in pyridine-iodoboranes increases linearly as the  $pK_a$  of the donor increases, for sterically similar donors.

It is notable that the slope of the plot in Figure 57 ( $-1.01$  Kcal/mole per  $pK_a$  unit) is steeper than that of an analogous plot for  $-\Delta(\Delta H_2)_{\text{R-py}}$  vs.  $pK_a$  where the slope is  $-0.66$  Kcal/mole per  $pK_a$  unit.<sup>67</sup> That is, the boron-nitrogen coordinate bond enthalpy increases more, for a given change in base strength of the donor, for pyridine-iodoboranes than pyridine-boranes. As a Lewis acid,  $\text{BH}_2\text{I}$  is more sensitive to changes in base strength of the donor than is  $\text{BH}_3$ . In this respect,  $\text{BH}_2\text{I}$  is intermediate in behavior between  $\text{BH}_3$  and the proton. A plot of  $\Delta(\Delta H)_{\text{R-py}}$  for the reaction of pyridines with methanesulfonic acid



has a slope of  $-1.5$  Kcal/mole per  $pK_a$  unit.<sup>66,67</sup> This suggests that  $\text{BH}_2\text{I}$  may have some "protonic character" in these adducts that  $\text{BH}_3$  does not possess. This character may exist

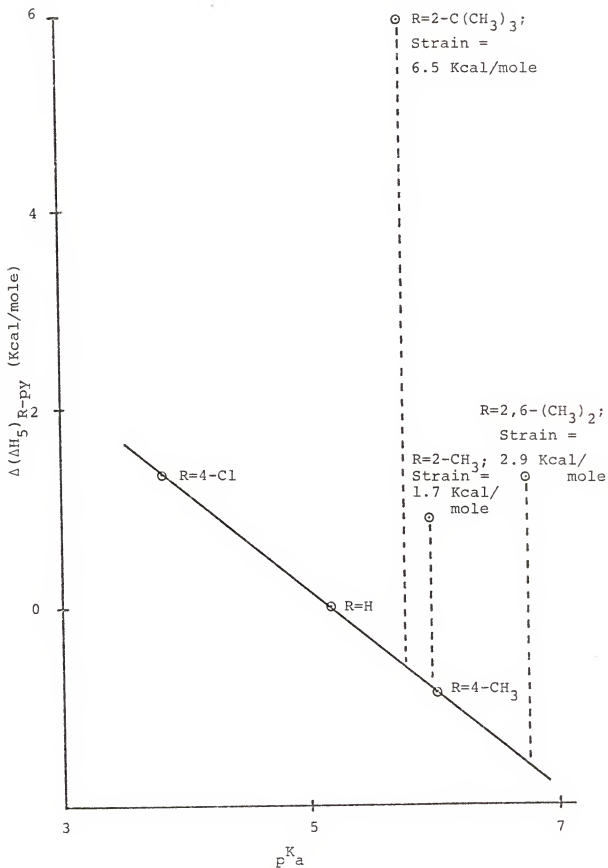


Figure 57. Relationship between the strengths of pyridine bases and their relative heats of reaction with iodoborane.

as a more compact acceptor orbital involved in the dative bonding to  $\text{BH}_2\text{I}$ , and/or more partial positive charge on the boron atom in  $\text{BH}_2\text{I}$  than in  $\text{BH}_3$ .

The position of equilibrium 47 can be readily interpreted in terms of the relative sensitivities of  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  to changes in base strength. Reaction to the right can be envisioned as a change in coordination of  $\text{BH}_3$  from the stronger base to the weaker base (an endothermic process), accompanied by a change in coordination of  $\text{BH}_2\text{I}$  from the weaker base to the stronger base (an exothermic process). Since  $\text{BH}_2\text{I}$  is more sensitive to changes in base strength than  $\text{BH}_3$ , the enthalpy decrease realized by the latter transformation more than compensates for the enthalpy increase of the former. Thus, reaction to the right is exothermic, and since  $K_{\text{eq}}$  is proportional to  $-\Delta H$  of reaction 47, the equilibrium constant is greater than one. Equilibrium is favored with the stronger base coordinated to  $\text{BH}_2\text{I}$ . More quantitatively, for 4-methylpyridine and 4-chloropyridine in equation 47, there is a difference of approximately 2.2  $\text{p}K_{\text{a}}$  units in base strength. Based on the slopes of the  $\Delta(\Delta H_2)_{\text{R-py}}$  and  $\Delta(\Delta H_3)_{\text{R-py}}$  plots ( $-0.66$  and  $-1.01$  Kcal/mole per  $\text{p}K_{\text{a}}$  unit, respectively), reaction to the right should have an enthalpy change of approximately

$$\Delta H = (-0.66 \frac{\text{Kcal/mole}}{\text{p}K_{\text{a}} \text{ unit}})(-2.2 \text{ p}K_{\text{a}} \text{ units}) +$$

$$(-1.0 \frac{\text{Kcal/mole}}{\text{p}K_{\text{a}} \text{ unit}})(2.2 \text{ p}K_{\text{a}} \text{ units}) = -0.7 \frac{\text{Kcal}}{\text{mole}}$$

This value is in good agreement with the enthalpy difference calculated from the observed equilibrium constant ( $K_{eq}' = 3.07$ ) and equation 49 ( $\Delta H = -0.69 \frac{\text{Kcal}}{\text{mole}}$ ).

Steric effects on the boron-nitrogen coordinate bond enthalpies in pyridine-iodoboranes can be ascertained by further examination of Figure 57. It is apparent that the data points for the pyridine derivatives with ortho alkyl substituents lie above the plot defined by the unhindered donors. For these amines, the heat liberated on reaction with  $\text{BH}_2\text{I}$  is less than expected on the basis of base strength. Alternatively, the boron-nitrogen coordinate bond enthalpies in those pyridine-iodoborane adducts are less than expected. Brown made similar observations for plots of  $-\Delta(\Delta H_2)_{\text{R-py}}$  vs.  $pK_a$ , and he attributed the discrepancies to steric interactions between the ortho ring substituents and the  $\text{BH}_3$  moiety. For each ortho-substituted pyridine, the vertical distance by which the data point lay above the plot determined by the unhindered pyridines was defined as the strain in the adduct. A similar definition is employed here. From Figure 57 it is apparent that the strains observed here for the ortho-substituted pyridine-iodoboranes are 1.7, 2.9, and 6.3 Kcal/mole, respectively, for 2-methyl, 2,6-dimethyl and 2-t-butyl substitution. Table 21 provides a comparison of these strains with those determined by Brown for other Lewis acids.

The difference in the strains of 2-methylpyridine with  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  (0.4 Kcal/mole) correlated closely with the observed discrepancies of the exchange equilibrium constants

Table 21  
Strains in Ortho-Substituted Pyridine Adducts with Boron Lewis Acids

Lewis Acid	2-CH <sub>3</sub> py Strain (Kcal/mole)	2,6-(CH <sub>3</sub> ) <sub>2</sub> py Strain (Kcal/mole)	2-C(CH <sub>3</sub> ) <sub>3</sub> py Strain (Kcal/mole)
BH <sub>3</sub> <sup>a</sup>	1.3	2.7	6.3
BF <sub>3</sub> <sup>a</sup>	2.2	8.5	10.5
BH <sub>2</sub> I	1.7	2.9	6.5

<sup>a</sup> Reference 67

( $K_{eq}$  and  $K_{eq}''$ ) for 2-methylpyridine-borane vs. 4-methylpyridine-borane. The slightly greater strain in 2-methylpyridine-iodoborane vs. 2-methylpyridine-borane forces the equilibria to the left relative to their positions for the 4-methylpyridine system as an unstrained standard. Similar observations can be made for the 2,6-dimethylpyridine and 2-t-butylpyridine systems, in that the degree to which the exchange equilibria are shifted to the left relative to the unstrained derivatives can be correlated with the difference in strain for the corresponding pyridine-borane and pyridine-iodoborane.

Thus, the relative positions of exchange equilibria 37, 47, and 48 can be interpreted in terms of the relative sensitivities of borane and iodoborane to changes in the electronic and steric properties of the pyridine donor molecules.

The most striking feature of Table 21 is actually the remarkable similarity of the strains in  $BH_3$  and  $BH_2I$  adducts with the same donors. More strain might be expected between  $BH_2I$  and ortho alkyl groups than with  $BH_3$ , due to the larger size of the iodine atom vs. the hydrogen atom. However, the observed differences in strain for  $BH_2I$  vs.  $BH_3$  are small for all three ortho-substituted pyridines. An explanation of this unexpected similarity in strains is offered in the following conformational analysis.

For a pyridine donor complexed to an unsymmetrical acceptor,  $BX_2Y$ , the most favorable conformation would be one which allows maximum separation of the bulkiest boron substi-



tuent (Y) from the ortho ring positions. As illustrated in Figure 58, this conformer would have a dihedral angle ( $\alpha$ ) of  $90^\circ$  between the plane defined by the boron, nitrogen and Y atoms and the plane of the pyridine ring. Actually, this conformation is probably also favored for adducts of symmetrical acids,  $BX_3$ , since it allows minimal eclipsing between substituents on boron and the ortho ring positions. For the pyridine adducts of the unsymmetrical acid,  $BH_2I$ , the iodine atom would occupy position Y, above the plane of the aromatic ring. In this conformation, there is virtually no steric interaction between the iodine atom and ortho alkyl groups, even for the bulky 2-t-butyl substituent. The effects of increasing the steric bulk of the ortho ring substituents are experienced only by the hydrogen atoms on boron. Positions X in Figure 58 are partially eclipsed by the ortho ring substituents and are consequently sensitive to changes in the steric requirements of these groups. Since a similar conformation is expected for pyridine-boranes, borane and iodoborane are sterically identical with respect to pyridine donors, as long as the iodine atom in  $BH_2I$  resides above the plane of the ring at position Y.

By contrast, in Brown's studies the strains in the pyridine- $BX_3$  adducts increased regularly as the steric bulk of the boron substituents increased. However, in these investigations all of the acids employed were symmetrical. That is, progressing from one acid to another, all three boron

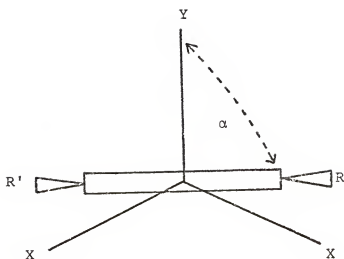


Figure 58. View of a pyridine adduct of an unsymmetrical boron Lewis acid ( $\text{BX}_2\text{Y}$ ) along the boron-nitrogen bond axis.

substituents were altered. Thus, the bulk of the two substituents on boron eclipsing the ortho ring positions were altered as well as that of the substituent on boron above the plane of the ring. Consequently, variations in strain with substitution on boron were unavoidable.

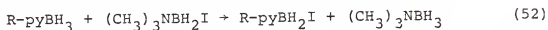
In summary, it appears that the following conclusions can be drawn with respect to the relative acceptor abilities of  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  toward pyridine donors. Electronically,  $\text{BH}_2\text{I}$  is a stronger acid than  $\text{BH}_3$  since it is more sensitive to changes in the base strength of the donor. The enhanced sensitivity of  $\text{BH}_2\text{I}$  might reflect a more positive boron atom or a less diffuse bonding orbital than for  $\text{BH}_3$ . Sterically,  $\text{BH}_2\text{I}$  and  $\text{BH}_3$  are very similar in their acceptor properties, even toward bulky pyridine donors. Consequently, considering steric and electronic effects,  $\text{BH}_2\text{I}$  is a stronger acid toward pyridine donors than  $\text{BH}_3$ . This conclusion is consistent with the observed greater acidity of  $\text{BI}_3$  vs.  $\text{BH}_3$  toward amine donors.

In a number of publications,<sup>63,67,68</sup> Brown and coworkers have successfully correlated the observed strains in pyridine adducts with  $\text{BH}_3$  and  $\text{B}(\text{CH}_3)_3$  with those in homomorphous organic compounds. Homomorphs are molecules having the same or closely similar molecular dimensions. Since the dimensions and geometry of the boron-nitrogen bond in amine-boranes are nearly identical with those of a carbon-carbon single bond, amine-boranes are homomorphs of hydrocarbons. For example, 2-t-butylpyridine-borane is a homomorph of o-t-butyltoluene. Brown

has presented considerable data supporting the postulate that the strains observed in boron-nitrogen addition compounds are also present in related organic molecules of similar sizes and shapes, and that the strains profoundly modify the chemical behavior of these substances. The strained pyridine-iodoborane derivatives investigated here are homomorphs of ortho-substituted benzyl iodides. The analysis presented here for pyridine-iodoboranes offers the opportunity to judge the chemical behavior of these organic compounds qualitatively, and perhaps quantitatively, in terms of the strains they are believed to contain by analogy with their inorganic homomorphs.

#### Kinetics of Hydrogen-Halogen Exchange

The observation of facile hydrogen-iodine exchange between a pyridine-borane and trimethylamine-iodoborane (reaction 52) offered the opportunity for the first rate study of a redistribution process between two saturated boron atoms, and the first mechanistic study of any type for the exchange of substituents between two neutral boron complexes.



The system also appeared suitable for testing the hypothesis that exchange of substituents between two coordinatively saturated boron atoms can occur only via predissociation to a trigonal boron species.

In order to gain some pertinent data with respect to the mechanism of hydrogen-halogen exchange at four-coordinate

boron, a kinetic study of reaction 52 was conducted. The rate law for the reaction, which describes the dependence of rate on reactant concentrations, is expected to be of the form

$$\text{rate (v)} = \frac{-d[\text{R-pyBH}_3]}{dt} = \frac{+d[(\text{CH}_3)_3\text{NBH}_3]}{dt} = k[\text{R-pyBH}_3]^m [(\text{CH}_3)_3\text{NBH}_2\text{I}]^n \quad (53)$$

where  $m$  and  $n$ , the order of the reaction with respect to reactant concentrations, are expected to be small positive integers, and  $k$ , the reaction rate constant, is a proportionality constant that relates the rate of the reaction to the concentrations of the reactants. The rate of disappearance of a reactant in equation 52 is equal to the rate of appearance of a product, and is expected to be proportional to integral powers of reactant concentrations at a constant temperature. Taking the logarithms of each side, equation 53 becomes

$$\log V = \log k + \log[\text{R-pyBH}_3]^m + \log[(\text{CH}_3)_3\text{NBH}_2\text{I}]^n, \text{ or} \\ \log V = \log K + m \log[\text{R-pyBH}_3] + n \log[(\text{CH}_3)_3\text{NBH}_2\text{I}] \quad (54)$$

Since  $n$  is a constant, then equation 54 reduces to

$$\log V = m \log[\text{R-pyBH}_3] + \text{constant} \quad (55)$$

where constant =  $\log k + n \log[(\text{CH}_3)_3\text{NBH}_2\text{I}]$ , if  $\log[(\text{CH}_3)_3\text{NBH}_2\text{I}]$  is also a constant. Consequently,  $m$ , the order of the reaction with respect to the pyridine-borane, can be determined by measuring variations in  $V$  as  $[\text{R-pyBH}_3]$  is altered at constant  $[(\text{CH}_3)_3\text{NBH}_2\text{I}]$ . A log-log plot of the resulting data

should have a slope equal to  $m$ . Likewise, a similar equation can be derived relating  $\log V$  to  $\log [(\text{CH}_3)_3\text{NBH}_2\text{I}]$  at constant pyridine-borane concentration

$$\log V = n \log [(\text{CH}_3)_3\text{NBH}_2\text{I}] + \text{constant}' \quad (56)$$

where  $\text{constant}' = \log k + m \log [\text{R-pyBH}_3]$ , and  $n$  can be determined from the slope at a plot of  $\log V$  vs.  $\log [(\text{CH}_3)_3\text{NBH}_2\text{I}]$ . Thus, the order of reaction 52 with respect to each reagent can be determined by measuring variations in the instantaneous rate ( $V$ ) of the reaction as the concentration of one reactant is altered at some constant concentration of the other reagent.

The order of reaction 52 with respect to each reagent was determined for pyridine-borane in methylene chloride at 35°C from plots of trimethylamine-borane concentration vs. time (Figures 1 - 7). Each figure represents one run with unique initial concentrations. The concentration of trimethylamine-borane at each time was determined by integration of the  $^1\text{H}$  nmr spectra of the reaction mixtures. Each reaction was examined sufficiently far from equilibrium (reaction 37) that the effects of the reverse reaction on the kinetic analysis could be ignored. Even for those runs which proceeded to 40% reaction based on the limiting reagent, the rate of the reverse reaction was never more than 0.03 times that of the reaction under investigation.

The instantaneous rate ( $V$ ) of the reaction at any point on the concentration vs. time plot is the slope of the tan-

gent to the curve at that point. The concentrations of the reactants corresponding to any point of tangency can be found directly from the trimethylamine-borane concentration according to the stoichiometry requirements of reaction 52.

$$[\text{pyBH}_3] = [\text{pyBH}_3]_0 - [(\text{CH}_3)_3\text{NBH}_3] \quad (57)$$

and

$$[(\text{CH}_3)_3\text{NBH}_2\text{I}] = [(\text{CH}_3)_3\text{NBH}_2\text{I}]_0 - [(\text{CH}_3)_3\text{NBH}_3] \quad (58)$$

In Figures 1 through 7, rates were determined from the slopes of tangents at trimethylamine-borane concentrations of 0.050 M. In each of the runs represented by Figures 1 through 4, the initial concentration of trimethylamine-iodoborane was constant (0.500 M), and therefore the concentration was constant (0.450 M). However, for each of these runs, the initial concentration of pyridine-borane was different, so the concentration of pyridine-borane at the point of tangency was unique, and any variation observed in  $V$  can be attributed to dependence on pyridine-borane concentration. Figure 8 represents a plot of  $\log V$  vs.  $\log[\text{pyBH}_3]$  at the points of tangency. According to equation 55, the line has a slope (1.03) equal to  $m$ , the order of the reaction with respect to pyridine-borane.

A similar analysis was employed to determine  $n$ , the order with respect to trimethylamine-iodoborane, from runs with constant initial concentrations of pyridine-borane (0.500 M) and variable initial concentrations of trimethylamine-iodoborane (Figures 1, and 5 - 7). The slope (1.04) of

the corresponding  $\log V$  vs.  $\log[(\text{CH}_3)_3\text{NBH}_2\text{I}]$  plot in Figure 9 is equal to  $n$ .

Assuming integral values only for  $m$  and  $n$  it is apparent that the reaction is first order with respect to each reagent.

Thus equation 53 may be rewritten as

$$\text{rate } (V) = \frac{dx}{dt} = k_2 (a_0 - x) (b_0 - x) \quad (59)$$

where  $x$  is the concentration of product,  $a_0$  is the initial concentration of trimethylamine-iodoborane, and  $k_2$  is the second order rate constant. This expression can be integrated by separating the variables. If  $a_0 \neq b_0$  the integrated rate expression is

$$k_2 t = \frac{1}{a_0 - b_0} \ln \frac{b_0 (a_0 - x)}{a_0 (b_0 - x)} \quad (60)$$

and if  $a_0 = b_0$ , the integrated rate expression is

$$k_2 t = \frac{x}{a_0 (a_0 - x)} \quad (61)$$

In either case, it is apparent that a plot of the right side of the equation vs. time ( $t$ ) will be linear with a slope equal to  $k_2$ , the second order rate constant. Such plots are referred to as second order plots, and the determination of rate constants and the substantiation of reaction orders by use of these plots are known as the integral graphical method of analysis. Figures 10 through 16 are second order plots for the kinetic runs presented in Figures 1 through 7.



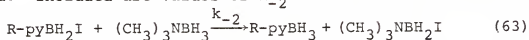
Several features of the second order plots suggest that the rate law proposed in equation 59 is correctly formulated over the extent of reaction examined. First, the data points generally adhere closely to the least squares plot with no observable drift and little scatter. The narrow range of the 95% confidence limits for the slope (Table 4) reflect this degree of precision. Secondly, each of the plots passes through, or very nearly through, the origin. Finally, the slopes (second order rate constants) of the seven plots are within good agreement of one another with a relative standard deviation (Sr) of 5.5%. The rate law

$$\text{rate} = k_2 [\text{R-pyBH}_3] [(\text{CH}_3)_3\text{NBH}_2\text{I}] \quad (62)$$

is applicable for pyridine-borane in methylene chloride with  $k_2 = 6.69 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$  at 35°C. It must be remembered, however, that this rate law will become invalid as the exchange reaction approaches equilibrium. A more rigorous treatment accounting for opposing second order reactions must be used to describe the kinetics of the reaction near equilibrium (see reference 69 for more details).

Kinetic runs were also conducted for substituted pyridine-borane derivatives in reaction 52 for 4-methyl, 4-chloro, 2-methyl, 2,6-dimethyl, and 2-t-butyl substitution at 35°C in methylene chloride. Again integrated  $^1\text{H}$  nmr spectra were used to follow changes in concentration with time. Figures 20 through 29 present second order plots of duplicate runs

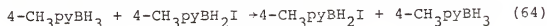
for each derivative. The least squares plots all pass through or near the origin, and their slopes have narrow 95% confidence limits, indicating that a second order rate law is also applicable for the substituted pyridine systems. The results of the least squares analysis are presented in Table 5. Table 6 lists the average second order rate constant for two or more runs for each pyridine-borane investigated. Included are values of  $k_{-2}$  for the reverse reaction



calculated from  $k_{-2} = k_2/K_{eq}$ , where  $K_{eq}$  is the equilibrium constant for the hydrogen-iodine exchange reaction (reaction 37). The most notable feature of the results summarized in Table 6 is the similarity in the magnitude of the second order rate constants for all of the pyridine derivatives investigated.

Although no systematic investigation of the temperature dependence of reaction 52 was undertaken, estimates of the activation parameters were made for 4-methyl substitution using an Arrhenius relationship and the second order rate constants at 35°C and 0°C. The activation enthalpy and entropy were approximated as 13 Kcal/mole and -31 cal/mole deg respectively, at 35°C.

A second order rate constant was estimated for reaction 64 in which hydrogen and iodine are exchanged between two complexes with the same donor molecule.



Since the reactant and products are identical, the method of  $^1\text{H}$  nmr integration used for determining the rate parameters of reaction 52 could not be employed here. Instead, the previously described temperature dependence of the  $^1\text{H}$  nmr spectrum of a mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane was employed. If the loss of resolution observed at room temperature is in fact due to a chemical exchange process, then at the temperature at which the 2,6-aromatic multiplets in Figure 50 have just broadened to a single resonance (approximately  $16^\circ\text{C}$ ), the average residence time ( $\tau$ ) for one of the 2,6-ring protons at a given site is  $\sqrt{2}/\pi J$ .<sup>70</sup> Since  $J$  is equal to 7 Hz for the 2,6-aromatic resonances of 4-methylpyridine-iodoborane,  $\tau$  is approximately equal to 0.064 sec. By analogy with reaction 52, the exchange process here is expected to be first order in each reactant. Then, since both solutes were present in equal concentrations, the mean lifetimes at each type of site were equal<sup>71</sup> and

$$\frac{1}{\tau} = k_2[4\text{-CH}_3\text{pyBH}_3] = k_2[4\text{-CH}_3\text{pyBH}_2\text{I}] \quad (65)$$

From reaction 65, and the approximate average residence time (0.064 sec),  $k_2$  was estimated as  $3 \times 10^1 \text{ M}^{-1} \text{ sec}^{-1}$ .

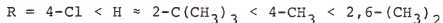
Assignment of some relative rates of reaction 66 were made by comparing the ambient temperature  $^1\text{H}$  nmr spectra of the pyridine-borane/pyridine-iodoborane mixtures (Figures 44 - 49).



For similar values of  $\Delta\delta$  ( $\Delta\delta = \delta_{R-pyBH_2I} - \delta_{R-pyBH_3}$ ), and similar coupling constants of the same resonance for two different pyridine derivatives, a greater extent of broadening and merge of the individual signals implies a faster rate of exchange.<sup>57,70</sup> For pyridine, 4-methylpyridine, 4-chloropyridine, and 2-t-butylpyridine, the values of  $\Delta\delta$  and  $J$  for the 2,6-aromatic resonances are similar (Tables 15 and 16). Examination of Figures 44, 45 and 48 and the corresponding spectrum for 2-t-butylpyridine (not shown), indicate that the degree of collapse and merge at comparable concentrations increases in the order  $4-Cl < H < 2-C(CH_3)_3 < 4-CH_3$ , suggesting a similar order for the rate of hydrogen-iodine exchange.

The information presented in Table 17 and Figure 49 permit some discussion of the relative rates of reaction 66 for the methyl substituted derivatives. Similar extents of methyl peak coalescence for two systems with different values of  $\Delta\delta$  implies a faster rate of exchange for the derivative with the larger  $\Delta\delta$ . For 2,6-dimethylpyridine,  $\Delta\delta$  (7Hz) is greater than for 4-methylpyridine ( $\Delta\delta$  equal to 3 Hz), yet both systems exhibit similar degrees of coalescence. Consequently, it appears that the exchange rate is greater for the 2,6-dimethylpyridine system than the 4-methylpyridine system. The methyl resonances for 2-methylpyridine are partially merged (Figure 49-C), but  $\Delta\delta$  (9Hz) is greater than for the other methyl derivatives, so that relative rate is difficult

to assign for this derivative. For the other systems, the spectra suggest the following order for the relative rates of reaction 66

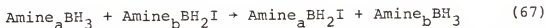


although these assignments are made with some reservations considering the method of analysis employed.

Perhaps the more significant point to be noted for the relative exchange rates (reaction 66) is not the differences in rates, but rather the similarity in the rates for all the pyridine derivatives examined in spite of considerable alterations in the steric and electronic properties of the donor molecule in the amine-borane and amine-iodoborane molecules. In all cases, the spectra have partially collapsed and merged, and since the frequency separations of  $\text{R-pyBH}_3$  and  $\text{R-pyBH}_2\text{I}$  are all of the same order of magnitude, the exchange rates are all of the same order of magnitude. For each substituent, the rate of hydrogen-iodine exchange corresponds to average lifetimes roughly equal to the observed frequency separations of the pyridine-borane and pyridine-iodoborane resonances, with second order rate constants of approximately  $10^1 \text{ M}^{-1} \text{ sec}^{-1}$ . Thus it appears that, as noted previously for reaction 52, the rate of reaction 66 is relatively insensitive to substituent changes on the pyridine donor molecule.

### Mechanism of Hydrogen-Halogen Exchange

Several mechanisms could be proposed for the hydrogen-iodine exchange reaction between two four-coordinate boron atoms



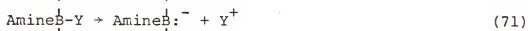
Any acceptable mechanism must be consistent with the experimental rate law, substituent effects, and other empirical data to be discussed subsequently, and should be compatible with the known chemistry of analogous systems. Two general classifications of mechanisms will be considered, based on whether the exchanging bonds to boron are broken and formed in a synchronous or stepwise fashion. In the first of these schemes, which will be referred to as dissociative, reaction is initiated by the cleavage of one of the four bonds to one (or both) of the boron atoms involved in the exchange. The second category, which is a nondissociative scheme, proceeds without cleavage of a bond to boron in a preliminary step, and thus requires the collision of two molecules with coordinatively saturated boron atoms in the rate-determining step.

Dissociative processes can be divided into two categories. First, there are those initiated by cleavage of the dative boron-nitrogen bond



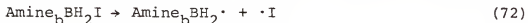
The amine-borane, the amine-iodoborane, or both species might be involved in this dissociation. Secondly, a boron-hydrogen

or boron-iodine bond might be cleaved in a preliminary dissociative step:



where Y is equal to H or I. As suggested by these equations, the B-Y bond could be broken in one of three fashions; homolytic cleavage, heterolytic cleavage to form a positively charged boron fragment, and heterolytic cleavage to form a negatively charged boron fragment. Considering the relative electronegativities of B and Y, and the lack of any precedent, reaction 71 is highly unlikely and will not be given any further discussion.

Homolytic cleavage (reaction 69) might proceed by the cleavage of a boron-hydrogen or a boron-iodine bond. Considering the relative B-Y bond energies,\* and the relative stabilities of the potential Y· radicals, the boron-iodine bond is more likely to undergo homolysis than the boron-hydrogen bond in the initiation step of a radical process.



It may be possible for a process initiated by reaction 72 to conform to the observed second order rate law, but neverthe-

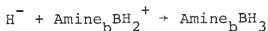
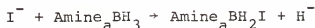
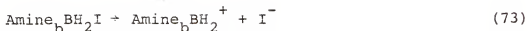
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\*The energy of a terminal boron-hydrogen bond in diborane is 93 Kcal/mole.<sup>64</sup> The boron-iodine bond energy in boron triiodide is 68 Kcal/mole including a  $\pi$ -bonding component.<sup>12</sup> The energy of a bond between iodine and tetrahedral boron should be less than this value, since  $\pi$ -bonding is less important in the adduct.

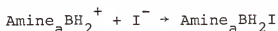
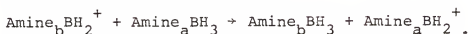
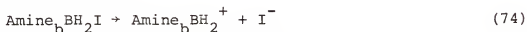
less it is not likely that the overall rate could exceed that of the initiation step. Even if a low boron-iodine bond energy of only 40 Kcal/mole is taken as the activation energy, and a high pre-exponential factor of  $10^{17}$  is assumed, a half-life for reaction 80 at 35°C in excess of  $10^7$  hr is calculated. The observed half-lives at 35°C for reactions 52 and 66 for initial 0.50 M concentrations are approximately 1 hr and  $10^{-5}$  hr, respectively. Consequently, a free radical mechanism for hydrogen-iodine exchange seems possible only if there are long radical chains. No induction periods were observed in the kinetic runs, and no EPR signal was detected in a solution of 1.0 M 4-methylpyridine-borane and 1.0 M 4-methylpyridine-iodoborane under conditions sensitive to radical concentrations as low as  $10^{-8}$  M. Thus, a radical exchange process seems unlikely.

Heterolytic cleavage reaction 70 is the ionization of a bond to boron to form dissociated ions, one of which is a potential nucleophile ( $Y^-$ ), and the other of which is a potential electrophile ( $\text{AmineBH}_2^+$ ). Considering the relative basicities of hydride ion vs. iodide ion, and the lack of a deuterium isotope effect on reaction 52, the ionization of the boron-iodine bond is more likely than the ionization of a boron-hydrogen bond. Once the ionic fragments have been formed, the exchange reaction might proceed by nucleophilic attack of iodide ion on  $\text{Amine}_a\text{BH}_3$ ,



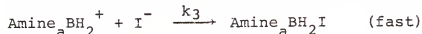
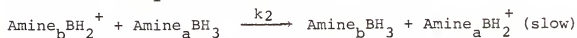
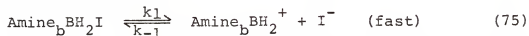


or by the electrophilic attack of the cationic boron fragment on  $\text{Amine}_a\text{BH}_3$ .



In either sequence, the net reaction is the observed hydrogen-iodine exchange.

Reaction sequence 73 is not a viable choice since it requires the displacement of the strongly basic hydride ion, and thus reaction scheme 74 remains as the only reasonable mechanism proceeding by preionization of a bond to boron. The experimental rate law (equation 62) for reaction 52 expresses concentration dependence on the amine-borane. Consequently, any proposed mechanism initiated by preionization of the boron-iodine bond, must have a subsequent step as the rate-determining one.



The first step is a rapid, reversible ionization of the boron-iodine bond to form dissociated ions, followed by rate-

determining electrophilic attack of the boron cation on the amine-borane molecule. Application of the steady state approximation to the intermediate cation produces a rate law which expresses concentration dependence on the amine-borane.

$$\text{rate} = \frac{k_1 k_2 [\text{Amine}_b \text{BH}_2 \text{I}] [\text{Amine}_a \text{BH}_3]}{k_{-1} [\text{I}^-] + K_2 [\text{Amine}_a \text{BH}_3]} \quad (76)$$

Since the second step is rate-determining, then  $k_2 [\text{Amine}_b \text{BH}_2^+][\text{Amine}_a \text{BH}_3] \ll k_{-1} [\text{Amine}_b \text{BH}_2 \text{I}]$ , and since the first step is an equilibrium

$$k_1 [\text{Amine}_b \text{BH}_2 \text{I}] = k_{-1} [\text{Amine}_b \text{BH}_2^+][\text{I}^-]$$

and then

$$k_2 [\text{Amine}_b \text{BH}_2^+][\text{Amine}_a \text{BH}_3] \ll k_{-1} [\text{Amine}_b \text{BH}_2^+][\text{I}^-]$$

or

$$k_2 [\text{Amine}_a \text{BH}_3] \ll k_{-1} [\text{I}^-]$$

In this case, the denominator of rate law 76 can be simplified to give

$$\text{rate} = \frac{k_1 k_2 [\text{Amine}_b \text{BH}_2 \text{I}] [\text{Amine}_a \text{BH}_3]}{k_{-1} [\text{I}^-]} \quad (77)$$

Although this rate law specifies the required concentration dependence with respect to the reactants, it also expresses inverse concentration dependence with respect to iodide ion. However, as long as the concentration of iodide ion remains constant during the exchange process, then the  $k_{-1} [\text{I}^-]$  term is constant, and the theoretical rate law complies with experimental rate law. Since the steps that com-

sume iodide ion in reaction scheme 75 (the  $k_{-1}$  and  $k_3$  steps) are fast, it is reasonable that  $[I^-]$  would rapidly achieve a steady state, and mechanism 75 would be acceptable, since rate law 77 would express the proper concentration dependencies.

The possible operation of this mechanism was tested directly by investigating the influence of large concentrations of externally added iodide ion on the rates of reactions 52 and 66. Rate law 77 requires that the rate of the exchange reaction would be decreased by added iodide ion via a mass law effect on the position of the ionization pre-equilibrium (common ion rate depression). The last three rows in Table 4 indicate that no common ion rate depression was observed for reaction 52 with concentrations of externally added iodide ion of up to 0.250 M. Likewise, the rate of reaction 66 (or the reverse reaction) appears to be insensitive to iodide concentration. Depression of the exchange rate would enhance the resolution of the separate  $^1\text{H}$  nmr resonances of the individual solutes as observed previously for low temperature spectra (Figures 50 and 51). However, the 4-methylpyridine resonances of a freshly prepared mixture of 0.50 M 4-methylpyridine-borane, 0.50 M 4-methylpyridine-iodoborane, and 1.02 M tetra-n-butylammonium iodide in methylene chloride at 35°C were essentially identical to those of an identical solution without externally added iodide ion (Figures 44 and 49-A). No resolution of the indi-

vidual resonances of the pyridine-borane and pyridine-iodoborane was observed. Likewise, no rate depression of reaction 66 was observed in the presence of 0.10 M triethylammonium iodide or 0.20 M bis(4-methylpyridine)boronium iodide. It is unlikely that the absence of common ion rate depression by externally added iodide salts can be attributed to ion-pairing of the added salt, which would effectively deactivate the mass effect of the iodide ion. Conductance data have demonstrated that the bis(pyridine)boronium iodide salt is not subject to extensive ion-pairing in the same solvent,<sup>72</sup> so significant ion-pairing is not likely for  $(4\text{-CH}_3\text{py})_2\text{BH}_2^+\text{I}^-$ . Thus, mechanism 75 is rejected for lack of compliance with the experimental rate law. The rate law for this scheme can exhibit dependence on the concentration of the amine-borane only if it also expresses an inverse dependence on the concentration of iodide ion, which is contrary to the experimental data.

Further evidence against the operation of mechanism 75 for reaction 52 is provided by the solvolysis data of Lowe and Kelly.<sup>48</sup> They reported an activation enthalpy of 17.2 Kcal/mole for the solvolysis of trimethylamine-iodoborane in aqueous dioxane via iodide displacement. The activation enthalpy of a mechanism initiated by the ionization of the boron-iodine bond in methylene chloride cannot be less than this value. In fact, a considerably greater activation enthalpy is expected for reaction 52 if it is initiated in this

fashion. In aqueous dioxane, the transition state should be stabilized by a dielectric and/or coordinative influence of the solvent, whereas in methylene chloride such stabilization is unlikely. The estimated activation enthalpy (13 Kcal/mole) for reaction 52 for 4-methyl substitution is actually less than Lowe's value. Thus, an exchange process initiated by heterolysis of the boron-iodine bond to dissociated ions can be excluded from consideration.

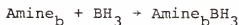
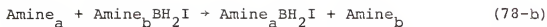
The one type of dissociation mechanism remaining for discussion is an exchange process initiated by the pre-dissociation of a boron-nitrogen dative bond (reaction 68). Reaction could proceed by the cleavage of the boron-nitrogen bond in the amine-borane (reaction 78-a) or in the amine-iodo-borane (reaction 79-a) to produce a free amine molecule and a three-coordinate boron species.\* In either event, the exchange process could be propagated by the nucleophilic attack of the liberated amine on a complex of four-coordinate boron (reaction 78-b and 79-b), or by the electrophilic attack of the free Lewis acid on a molecule of complex (reactions 78-c and 79-c), followed by recombination of Lewis acid and base fragments.



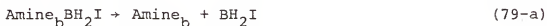
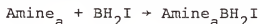
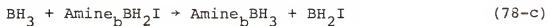

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\* Although it is expected that the free Lewis acids may be in equilibrium with their dimers, this complication will not be introduced as it has no bearing on the following analysis.

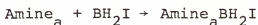
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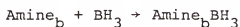
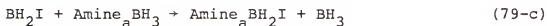
or



then



or



Exchange could also be accomplished by the predissociation of the boron-nitrogen bonds in both the amine-borane and the amine-iodoborane (reaction 78-a and 79-a) followed by recombination of the Lewis acid and base fragments (reactions 80-a and 80-b) in a process known as stepwise complex formation.<sup>1</sup>

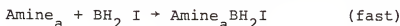
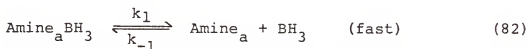


In order to comply with the observed second order rate law, any mechanism proceeding via boron-nitrogen bond predissociation must have as the rate-determining step some

process occurring after the dissociative step. Otherwise, the rate law would exhibit dependence on the concentration of one reactant only. It can be demonstrated that reaction schemes initiated by steps 78-a or 79-a can in fact comply with the experimental rate law if the dissociation is rapid and reversible, and if the concentrations of free Lewis acid and base remain small throughout the reaction. For example, a steady state analysis of reaction scheme 78-c provides the following rate law

$$\text{rate} = \frac{k_1 k_2 [\text{Amine}_a \text{BH}_3] [\text{Amine}_b \text{BH}_2 \text{I}]}{k_{-1} [\text{Amine}_a] + k_2 [\text{Amine}_b \text{BH}_2 \text{I}]} \quad (81)$$

for



Since the first step is rapid relative to the second, it can be shown that

$$k_{-1} [\text{Amine}_a] \gg k_2 [\text{Amine}_b \text{BH}_2 \text{I}]$$

and rate law 81 reduces to

$$\text{rate} = \frac{k_1 k_2 [\text{Amine}_a \text{BH}_3] [\text{Amine}_b \text{BH}_2 \text{I}]}{k_{-1} [\text{Amine}_a]} \quad (83)$$

Consequently, as long as the concentration of free Amine<sub>a</sub> remains low during the reaction (a reasonable supposition), the experimental rate law will be followed.

However, even though reaction scheme 82 can adhere to the experimental rate law, it can nevertheless be rejected on other grounds. The activation enthalpy for the reaction in a noncoordinating solvent such as methylene chloride could not be less than the boron-nitrogen coordinate enthalpy of the amine-borane. The boron-nitrogen coordinate bond enthalpy of the amine-borane could not be less in absolute value than the heat of reaction of Amine<sub>a</sub> with diborane. Brown's data for the heat of reaction of 4-methylpyridine with B<sub>2</sub>H<sub>6</sub> provide a value of approximately 33 Kcal/mole as a lower limit for the boron-nitrogen coordinate bond enthalpy in 4-methylpyridine-borane.<sup>63</sup> For the 4-methylpyridine derivative in reaction 52, the estimated activation enthalpy (13 Kcal/mole) is considerably lower than this value, and the activation enthalpy for reaction 66 must be lower yet. The rates of reactions 52 and 66 for the other derivatives are not much different than those for 4-methylpyridine, and the activation enthalpies are probably also quite similar (i.e. roughly 13 Kcal/mole). Thus, even 2-t-butylpyridine-borane, which has the lowest boron-nitrogen coordinate bond enthalpy of the amine-boranes studied here (26 Kcal/mole as a lower limit), cannot react via predissociation of the amine-borane into the Lewis acid and base.

Predissociation of the amine-borane can also be eliminated from consideration based on the experimental rate constants of reactions 52 and 66. Ryschkewitsch and Birnbaum



have measured the rates of solvolysis of several pyridine-boranes in n-propanol.<sup>65</sup> For each of the adducts studied, the activation enthalpy of the solvolysis reaction was 8-10 Kcal/mole less than the boron-nitrogen coordinate bond enthalpy deduced from Brown's thermochemical data,<sup>63</sup> suggesting involvement of the donor solvent in the transition state. Nevertheless, the propanolysis reactions were considerably slower than the hydrogen-iodine exchange reactions examined here, even though no comparable involvement of the solvent in the transition state is expected in methylene chloride. For example, extrapolation of an Arrhenius plot to 35°C predicts a half-life of approximately 170 hr for the propanolysis of 4-methylpyridine-borane. The half-lives observed for the exchange reactions 52 and 66 for 4-methylpyridine were 1 hr and  $10^{-5}$  hr, respectively, for 0.50 M concentrations of each reactant. Thus, the exchange reactions are too rapid to proceed via reaction 78-a as an initiation step.

The foregoing conclusions eliminating exchange schemes initiated by cleavage of the boron-nitrogen bond in the amine-borane are consistent with the reports of Benton<sup>14</sup> and Hartman<sup>16</sup> that the exchange of halogens between two boron trihalide adducts of trimethylamine does not occur even at elevated temperatures. For example, no halogen exchange occurred between trimethylamine-boron trifluoride and trimethylamine-boron trichloride on several hours of heating at 180°C in trichlorobenzene or nitrobenzene. Trimethylamine-boron tri-

fluoride and uncoordinated boron trichloride exchanged halogens rapidly in solution at room temperature. Thus, the inertness of the  $(\text{CH}_3)_3\text{NBF}_3/(\text{CH}_3)_3\text{NBCl}_3$  system to exchange can be attributed to the stability of the adducts to boron-nitrogen bond cleavage and not to some subsequent bottleneck in the reaction mechanism. Further, using isotopically labelled boron, Coyle has demonstrated that halogen exchange between an adduct of a tertiary amine and boron trifluoride and free boron trichloride occurs via boron-nitrogen cleavage only at elevated temperatures.<sup>18</sup> Considering the relative acceptor abilities of  $\text{BH}_3$  vs.  $\text{BF}_3$  toward amine donors ( $\text{BH}_3 > \text{BF}_3$ ), it is quite reasonable to conclude that the exchange processes studied herein do not proceed via cleavage of the dative boron-nitrogen bond in the amine-borane.\*

Exchange mechanisms initiated by cleavage of the boron-nitrogen dative bond in the amine-iodoborane (reaction 79) can also be discounted. In an earlier section of the Discussion, it was proposed that  $\text{BH}_2\text{I}$  is a stronger acceptor than  $\text{BH}_3$  toward nitrogen donors, and new evidence in support of this hypothesis was advanced. Consequently, it is expected that amine adducts of  $\text{BH}_2\text{I}$  are less susceptible to heterolytic boron-nitrogen bond cleavage than the  $\text{BH}_3$  adduct.

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\* This argument is based in part on the assumption that the relative activation enthalpies of heterolytic boron-nitrogen bond cleavage for two adducts can be inferred directly from the relative enthalpies of formation of the adducts from the free acid and base. The validity of this assumption will be demonstrated in a later section.

Since predissociation of the dative bond in the amine-borane has been eliminated from consideration, likewise cleavage of the boron-nitrogen bond in the amine-iodoborane in a preliminary step can also be excluded. Further, stepwise complex formation, which requires the energetically unfavorable cleavage of two dative bonds before exchange occurs, is untenable.

One other mechanistic scheme, which may be classified as a dissociative process, merits consideration. Boron Lewis acids have been observed to catalyze hydrogen-halogen exchange reactions. For example, boron tribromide catalyzes the hydrogen-halogen exchange reactions of benzhydryl and *t*-butyl halides with silane derivatives.<sup>73</sup> Further, although two trimethylamine adducts of boron trihalides fail to exchange substituents in solution even at elevated temperatures, an adduct will frequently exchange halogen readily with free boron trihalide, and an excess of Lewis acid can facilitate exchange between two adducts.<sup>14,16,21</sup> Since diborane, a Lewis acid, was known to be a product of a side reaction (reaction 43) inherent to the systems under investigation, the possibility of acid-catalyzed exchange was examined. Reaction 43 is expected to produce diborane whenever the pyridine-borane and pyridine-iodoborane are both present. Such a situation could arise for reaction 37 in three general ways. Catalytic quantities of diborane might result from a small extent of slow, uncatalyzed exchange followed by reac-

tion 43 and catalyzed exchange. Small quantities of diborane might also be present before the occurrence of any hydrogen-iodine exchange, the origin of the Lewis acid depending on whether the equilibrium was approached from the left side or right side of equation 37. When a solution of a pyridine-iodoborane is prepared by the reaction of iodine with the pyridine-borane, a transient mixture of the two reactants necessary for diborane production (via reaction 43) is unavoidable. Thus, when the iodoborane solution is mixed with a trimethylamine-borane solution, the initial reaction mixture will contain traces of diborane before any exchange occurs. Initial trace quantities of diborane might also be present when equilibrium is approached from the left side of equation 37. The in situ preparation of trimethylamine-iodoborane from stoichiometric quantities of trimethylamine-borane and iodine could conceivably leave traces of unreacted hydrogen iodide. When the pyridine-borane solution is added, its reaction with residual hydrogen iodide could produce the conditions necessary for the intrusion of diborane via reaction 43.\* However, only very small quantities of diborane could result from any of the aforementioned sources.

The results obtained for the 0°C runs for 4-methyl substitution in reaction 52 (Figures 31 - 32 and Table 5) sug-

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\* This possibility seems unlikely, since the exchange rate of reaction 52 was not altered by the use of an excess of trimethylamine-borane over the quantity of iodine required to produce trimethylamine-iodoborane

gest that diborane does not catalyze the hydrogen-iodine exchange reaction. A sample containing 25 mole % (based on reaction 43) of externally added diborane reacted at the same rate as a control sample without added diborane. A low reaction temperature of 0°C was especially suitable for this experiment, since reaction 43 is very slow at this temperature, minimizing the likelihood of any diborane production in the control sample.

Further evidence against acid-catalyzed exchange was provided by the nature of the  $^1\text{H}$  nmr spectrum of a sample of 4-methylpyridine-borane and 4-methylpyridine-iodoborane with 21 mole % of externally added diborane. The spectrum was essentially the same\* as that of a freshly prepared control sample without the added diborane (Figures 44-C and 49-A). Both samples exhibited spectra with the same extents of broadening and convergence of resonances. If diborane catalyzed exchange reaction 39 significantly, the spectrum of the sample with added diborane would display sharper signals for the 4-methylpyridine resonances than the control spectrum.

Thus, it may be concluded that the addition of large quantities of diborane does not affect the rates of the hydrogen-iodine exchange reactions. However, the postulate might be advanced that only a small, catalytic amount of diborane is required to accelerate the exchange process, and that the

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\* Minor differences will be discussed in a later section.

addition of the Lewis acid in excess of this small, rate-controlling quantity should have no effect on the rate. This suggestion would be a contradiction of the general observation that a large amount of free Lewis acid is necessary for a facile catalytic process.<sup>13</sup>

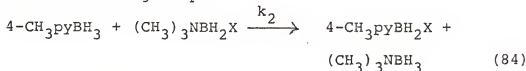
From the foregoing discussion, it can be concluded that the hydrogen-iodine redistribution reactions between two coordinatively saturated boron atoms do not proceed via any dissociative mechanism. Thus, it is evident that exchange must occur by the collision of two molecules of undissociated complex in a bimolecular reaction. Indeed, the activation parameters estimated for the 4-methyl derivative for reaction 52 support this conclusion. All of the bonds in the system are expected to have enthalpies in excess of 13 Kcal/mole, and thus it is evident that bond formation must be concomitant with bond cleavage in the transition state, indicative of a bimolecular process. Likewise, a highly negative entropy of activation (-31 cal/mole deg) is characteristic of a bimolecular transition state, and speaks against any unimolecular dissociation.

Amine-iodoboranes have been observed to react with a variety of nucleophiles with the displacement of iodide ion from boron.<sup>49,50,74,75</sup> Based on yield data, Nainan and Ryschewitsch concluded that, for amine nucleophiles, the reaction is a bimolecular displacement of iodide ion by the approaching donor. This proposal is analogous to the  $SN_2$  reaction

mechanism common for alkyl and aralkyl halides in organic chemistry.

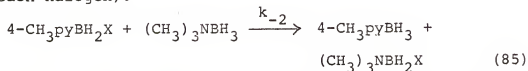
Amine-boranes, on the other hand, are subject to electrophilic attack on the boron-hydrogen bond. A variety of electrophilic reagents have been employed to substitute a boron-hydrogen with halogen.<sup>11,19,76,77</sup> Noeth<sup>19</sup> has described the boron-hydrogen bond as a nucleophile in these reactions.

Consequently, a mixture of an amine-borane and an amine-iodoborane contains a substrate susceptible to nucleophilic attack ( $\text{Amine}_b\text{BH}_2\text{I}$ ), and a potential nucleophile ( $\text{Amine}_a\text{BH}_3$ ). Alternatively, the amine-iodoborane may be viewed as an electrophile capable of abstracting a hydride ion from the boron atom of the amine-borane by analogy with other electrophilic reagents. From either viewpoint, a bimolecular reaction between an amine-iodoborane and the boron-hydrogen bond of an amine-borane seems quite feasible, and could account for the hydrogen-iodine exchange reactions observed here. Such a bimolecular exchange would proceed with the simultaneous loss of iodide from the amine-iodoborane and transferal of hydride from the amine-borane to the amine-iodoborane in the transition state. The dependence of the rate of reaction 84 on the halogen supports the hypothesis that halide ion is lost in the rate-determining step.



(X = Cl, Br, I)

The reluctance of the reaction to proceed for the bromo and chloro derivatives is, in fact, kinetic in origin, and not merely a reflection of unfavorable equilibria, since similar rates were observed for the reverse reactions (i.e.  $k_{-2} \approx k_2$  for each halogen).



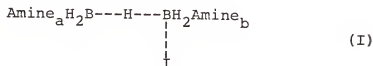
The order of reactivity ( $\text{I} > \text{Br} > \text{Cl}$ ) observed for reactions 84 and 85 is consistent with the relative boron-halogen bond strengths,<sup>6,60,78</sup> the relative leaving group abilities of the halide ions, and the relative ease of displacement of halide ion from boron with other nucleophiles. Ryschkewitsch has noted the same order of reactivity for the displacement of halide ion from tetrahedral boron with amine donors,<sup>79</sup> as have Lowe and Kelly<sup>48</sup> for the relative rates of solvolysis of trimethylamine-haloboranes in aqueous dioxane.

Transfer of hydride from the amine-borane to the amine-iodoborane via a bimolecular collision would require the formation of a three-center, two-electron, B-H-B bridge-bond in the transition state. The required vacant orbital at the boron atom of the amine-iodoborane would be provided by the simultaneous loss of iodide ion. Boron-hydrogen compounds are known to form B-H-B bridge-bonds quite readily, and, in some cases, stable species result.<sup>78</sup> Diborane has a structure with two bridges of this type between the boron atoms. Boron compounds are also known to form singly bridged structures



with only one B-H-B bond. Examples are the diborohydride anion ( $B_2H_7^-$ ), and the  $DonorBH_3 \cdot BH_3$  complexes, where ethers, pyridine, and trimethylamine are donors.<sup>36,80,81</sup> For amine donors, the adducts exist only at low temperatures, and they have been postulated as intermediates in the cleavage reactions of diborane with donors.<sup>36</sup>

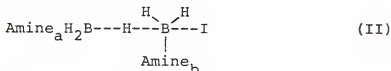
Electron-deficient B-H-B bridge-bonds may be proposed for the transition state of the hydrogen-iodine exchange reactions examined here.



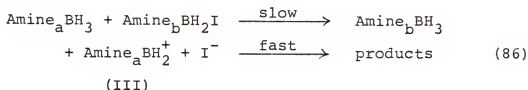
However, it must be recognized that structure I contains one boron atom involved in bonding to five other atoms. Since boron is a first row element, formation of the three-center, two-electron bond in the transition state requires the liberation of an orbital on the boron atom of the amine-iodoborane (hereafter referred to as boron atom b). Such unsaturation can be achieved in a bimolecular collision, only if the iodide ion leaves the coordination sphere of boron atom b as the nucleophile arrives.

There are two basic bimolecular reaction pathways by which such a synchronous bond cleavage and formation process could occur, each of which has precedents in the chemistry of tetrahedral boron compounds. The first of these, which is analogous to the  $SN_2$  reaction of organic halides, is the backside displacement of the iodide leaving group by the incoming,

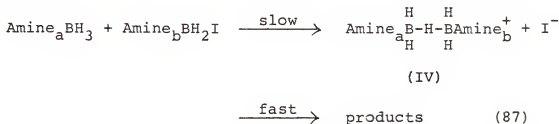
nucleophilic boron-hydrogen bond. The transition state (II) would be approximately trigonal bipyramidal around boron atom b, with the entering and leaving groups at axial positions, and with two hydrogen atoms and Amine<sub>b</sub> occupying the equatorial positions.<sup>82</sup>



The reaction might proceed via concerted iodide loss and hydride abstraction producing Amine<sub>b</sub>BH<sub>3</sub> and a three-coordinate boronium ion (III). The latter species would be expected to combine rapidly with displaced iodide ion to form Amine<sub>a</sub>BH<sub>2</sub>I.

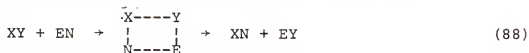


Alternatively, a bridged cationic intermediate (IV) might have sufficient stability to exist briefly before being subjected to bridge-bond cleavage by attack of the nucleophilic iodide ion.



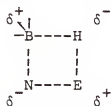
The second type of bimolecular reaction path to be considered proceeds via a cyclic transition state in a four-center reaction. Dessy defines a four-center mechanism (S<sub>F</sub>) as

one in which bonding changes occur simultaneously at four different sites in a cyclic system.<sup>83</sup> Four-center transition states have frequently been proposed for the reaction of a substrate (X-Y) with a bifunctional attacking species (E-N) with nucleophilic and electrophilic capabilities.



The electrophilic portion of the reagent (E) assists the nucleophilic attack of N on the substrate via simultaneous removal of Y<sup>-</sup>, the leaving group. At the same time, the nucleophilic portion of the attacking species (N) assists the electrophilic attack on Y by coordination to X in the transition state.

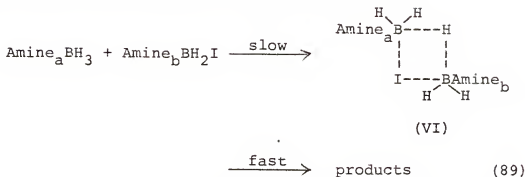
Four-center transition states (V) have been postulated for the reaction of the boron-hydrogen bonds of amine-boranes with a variety of reagents.



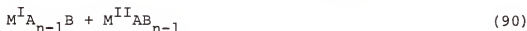
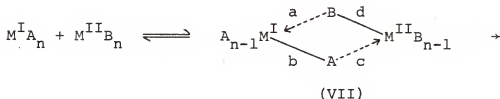
(V)

Transition states of this type have been proposed for the reactions of amine-boranes with halogens,<sup>19,84</sup> hydrogen halides,<sup>11,19,84</sup> boron trihalides,<sup>14,19</sup> aralkylhalides,<sup>77</sup> and a variety of other halides and oxyhalides.<sup>11</sup> An analogous transition state can be proposed for the reaction of an amine-

borane with an electrophilic amine-iodoborane.



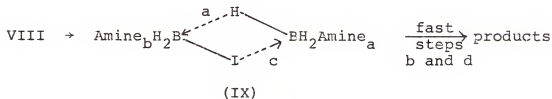
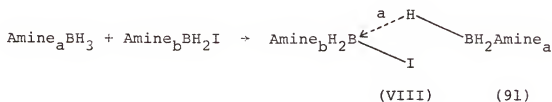
Lockhart<sup>1</sup> has proposed the operation of a four-center mechanism for the exchange reactions of a variety of central atoms ( $\text{M}^{\text{I}}$  and  $\text{M}^{\text{II}}$ ), and a number of exchanging groups (A and B)



Steps a and c are bond formation processes in which A and B act as donors toward the respective central atoms. In general, the greater the acceptor powers of  $\text{M}^{\text{I}}$  and  $\text{M}^{\text{II}}$ , and the greater the donor abilities of A and B, the faster the redistribution process occurs. The bond formation and cleavage steps can occur in a stepwise fashion. In particular, if  $\text{M}^{\text{I}}$  is a better acceptor than  $\text{M}^{\text{II}}$ , and if B is a better donor than A, then reaction will be initiated by step a, the nucleophilic attack of donor B on acceptor  $\text{M}^{\text{I}}$ . In that case, the intermediate formed should have reduced acceptor power at  $\text{M}^{\text{I}}$ , but increased acceptor power at  $\text{M}^{\text{II}}$ . At the same time, the  $\text{M}^{\text{I}}$ -A bond is

weakened, increasing the nucleophilicity of A. Consequently, step c, the formation of the  $M^{II}$ -A bond is facilitated. Formation of the  $M^I$ -B bond enhances the acceptor ability of  $M^{II}$  and the donor ability of A. Finally, cleavage steps b and d lead to the redistributed products.

In the system under investigation here, the central boron atom in the amine-iodoborane undoubtedly has greater acceptor ability than the boron atom in the amine-borane, as evidenced by the relative reactivities of the two substrates toward nucleophiles such as amines. Further, hydrogen is a better donor than iodine toward boron, and also displays a propensity for bridge-bond formation. Thus, a four-center process initiated by the formation of a bridge boron-hydrogen bond from the amine-borane to the amine-iodoborane is reasonable (structure VIII). Such coordination would increase the acceptor ability of the boron atom of the amine-borane (hereafter referred to as boron atom a), and would enhance the nucleophilicity of iodine through a weakening of the B-I bond. Thus, step a facilitates step c in forming the four-center structure IX.

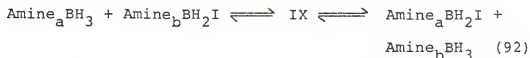


In this respect, the amine-iodoborane can be envisioned as a bifunctional reagent as formulated by Dessy.<sup>83</sup> Conceptually, transition state IX can be envisioned as intermediate between the extremes of nucleophilic attack of iodide ion on the amine-borane with the displacement of hydride, and electrophilic attack of  $\text{Amine}_2\text{BH}_2^+$  on the B-H bond of the amine-borane. Neither the nucleophilic nor the electrophilic attack could proceed alone, since hydride ion is a poor leaving group, and since the amine-iodoborane does not dissociate into ions. However, the two modes of attack can assist each other in a concerted reaction via transition state IX.

In the ensuing discussion, the relative suitabilities of the  $\text{SN}_2$  mechanism (reaction schemes 86 and 87) and the  $\text{S}_\text{F}$  mechanism (reaction scheme 91) for the hydrogen-iodine exchange reaction will be considered. Each of the bimolecular pathways will be weighed with respect to several criteria, including compatibility with the observed second order rate law, substituent changes on the donors, substituent changes on boron (i.e. deuterium for hydrogen substitution, and variation of the halogen), and the estimated activation parameters. In addition, the necessity for unsaturation at the boron atom of the iodoborane and the principle of microscopic reversibility will be considered.

The  $\text{S}_\text{F}$  mechanism and both of the possible  $\text{SN}_2$  mechanisms proceed via a bimolecular collision in the rate-determining step followed by a rapid decay to the products. Thus, all

three reaction paths are consistent with the experimentally determined rate law for hydrogen-iodine exchange (equation 62). The hydrogen-iodine exchange reactions are reversible, and according to the principle of microscopic reversibility, exchange from either direction must proceed along the same reaction coordinate via the same intermediates. The transition state for the  $S_F$  mechanism (structure IX) is suitable for exchange from either direction.



The only difference between the transition states for the forward and reverse reactions is the movement of charge in the four-center cyclic transition state. Negative charge is transferred in a counterclockwise fashion around the reaction centers in structure IX for the forward reaction, and in a clockwise direction for the reverse reaction.

The singly bridged intermediate (IV) in reaction scheme 87 is similarly suited for reaction in either direction. The observation of a net change in either the forward or reverse direction would depend only on which boron-hydrogen bridge bond is cleaved by the nucleophilic iodide ion. Reaction scheme 86 can be rejected, since the microscopic reversibility principle requires that the reverse reaction proceed by preionization of the boron-iodine bond in  $\text{Amine}_a\text{BH}_2\text{I}$ , a reaction path already excluded from consideration on the basis of experimental data. Thus, reaction sequence 87 is the only viable  $\text{SN}_2$  process, and further mention of the  $\text{SN}_2$  mechanism

refers to this pathway.

The  $S_F$  and  $SN_2$  mechanisms each require the formation of a three-center, two-electron B-H-B bond. Bonds of this type are common in boron compounds with each of the participating atoms contributing one orbital to the bridge bond. Since the boron atom of the amine-iodoborane is coordinatively saturated, bridge bond formation can occur in the transition state only to the extent that an orbital on this boron atom is liberated. The  $SN_2$  mechanism is readily analyzed within this limitation. The  $sp^2$ -hybridized boron atom in the trigonal bipyramidal transition state has one lobe of a 2p orbital directed toward the leaving iodide ion and the other lobe toward the incoming boron-hydrogen bond.<sup>82</sup> The three-center bond would involve a 2p orbital on boron atom b, a  $sp^3$ -hybridized orbital on boron atom a, and a 1s orbital on hydrogen. Except for the participation of a 2p rather than a  $sp^3$  orbital on one boron atom, this bonding scheme is no different than that of a B-H-B bridge bond of diborane. The involvement of a 2p orbital on boron in three-center bonding has precedents in the accepted description of the bonding arrangements in  $B_5H_9$  and other boron hydrides.<sup>78</sup> Progression along the reaction coordinate to structure IV would produce a conventional B-H-B bridge bond between two  $sp^3$ -hybridized boron atoms. Thus, the accepted view of the  $SN_2$  mechanism provides the unsaturation at the boron atom of the iodoborane necessary for bimolecular exchange.

The  $S_F$  mechanism also requires the generation of unsatu-



ration at boron atom b for bridge bond formation. Again, this condition could be fulfilled if the iodide ion leaves the coordination sphere of boron atom b as the nucleophile arrives. However, in contrast to the  $SN_2$  mechanism, the orbital rearrangements involved in  $S_F$  reactions at saturated centers have not been well formulated. Cyclic four-center exchange can be described in terms of conventional bonding schemes if amine-iodoboranes exist as ion pairs,  $\text{amineBH}_2^+\text{I}^-$ . The boron atom in such a species would have an orbital available for bridge bond formation with the amine-borane nucleophile. During the exchange process, the iodide ion would enter into electrovalent bond formation with boron atom a as orbital unsaturation was generated there by hydride loss.

Winstein<sup>85</sup> defines the intimate ion pair in solution as two ions of opposite charge in contact, with no intervening solvent molecules. Ion pairs have been identified as intermediates in the reactions of alkyl halides with nucleophiles.<sup>85-88</sup> By analogy, nucleophilic attack of an amine-borane on an amine-iodoborane might proceed via an ion pair intermediate derived from the amine-iodoborane.

Kosower has proposed that the ground state of the charge transfer complex formed between the N-methylpyridinium cation and the iodide anion may be depicted as an intimate ion pair.<sup>89</sup> The iodide ion is believed to reside above the plane of the pyridinium ring near the nitrogen atom which is the centroid

of positive charge. An intimate ion pair derived from pyridine-iodoborane would be a close analog of the ground state of the N-methylpyridinium iodide charge transfer complex, with the N-methyl group substituted with  $\text{BH}_2$ .

Earlier in this study, it was proposed that the most stable conformers of the  $\text{BH}_2\text{I}$  adducts of pyridine donors would have the iodine moiety positioned above a plane containing the pyridine ring and the boron atom (i.e.  $\alpha = 90^\circ$  in Figure 58). In this case, the formation of an ion pair analogous to the ground state of the N-methylpyridinium iodide complex merely requires the migration of the iodide ion involved in electrovalent bonding to boron a short distance toward the nitrogen atom. In fact, the iodide ion may reside close to the boron-nitrogen bonding region in the ground state of a charge transfer complex, since some of the positive charge on the pyridinium cation should be transferred to the relatively electropositive boron atom.

The ultraviolet spectra of some substituted pyridine-iodoboranes in solvents of low polarity suggest that these compounds do in fact exist as tight ion pairs. The ultraviolet spectra of 4-chloropyridine-borane and 4-chloropyridine-iodoborane in methylene chloride are presented in Figure 54. The spectrum of the iodinated derivative is generally more intense, particularly near 292 nm and 240 nm, and  $\lambda_{\text{max}}$  has shifted to shorter wavelength. The enhanced absorbance near 292 nm appears as a broad shoulder of medium intensity on the red side of the main absorption maximum. No

corresponding shoulder appears in the spectrum of 4-chloropyridine-borane. Similar differences were observed between the spectra of 4-methylpyridine-borane and 4-methylpyridine-iodoborane, although the broad shoulder on the red side of the main peak was not as well resolved for 4-methylpyridine-iodoborane as for 4-chloropyridine-iodoborane.

The additional broad absorption observed for the pyridine-iodoborane derivatives is assigned as a charge transfer transition from the iodide ion to the  $R\text{-pyBH}_2^+$  cation of a tight ion pair. The solvent and substituent effects on the position of this transition, and the appearance of another broad absorption at shorter wavelength are consistent with this assignment.

Kosower has intensively investigated solvent effects on the charge transfer spectra of substituted N-methylpyridinium iodides.<sup>89</sup> The charge transfer band moves to higher energy as the polarity of the solvent is increased. In the ground state of the complex, the iodide ion is above the pyridinium ring, and the dipole of the complex is perpendicular to the ring. Upon the absorption of light, the complex is transformed to the excited state which has a dipole moment perpendicular to that of the ground state. In the ground state, the complex is stabilized by interaction with solvent dipoles. According to the Franck-Condon principle, the electronic charge transfer transition is so rapid that no molecular motion can occur. Solvent molecules are unable to reorien-

tate themselves around the changed dipole, and the excited state is destabilized relative to the ground state. As solvent polarity increases, the stabilization of the ground state relative to the excited state is enhanced, and the energy change ( $\Delta E_{CT}$ ) of the charge transfer transition increases. In fact, Kosower has employed the energy of the charge transfer transition for 1-ethyl-4-carbomethoxyppyridinium iodide in a given solvent as a measure of solvent polarity,  $Z$ , where  $Z$  is  $\Delta E_{CT}$  in that solvent.<sup>89</sup> A larger value of  $Z$  indicates a more polar solvent.

The effect of a change in solvent from cyclohexane ( $z = 60.1$ )\* to methylene chloride ( $z = 64.2$ ) on the ultraviolet spectrum of 4-methylpyridine-iodoborane is illustrated in Figure 55. The broad absorption at the red end of the spectrum shifts to shorter wavelength as the polarity of the solvent increases, consistent with the assignment of this absorption to a charge transfer transition. Likewise, the magnitude of the solvent shift is comparable to the shift observed for the charge transfer band of 4-methyl-N-methylpyridinium iodide for a similar change in solvent polarity. Kosower has concluded that similar sensitivities to solvent changes for different substituted pyridinium iodides indicate that the ground states of the complexes for the two systems

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\* No  $Z$  value has been determined for cyclohexane, but it is expected to be similar to that of isooctane for which  $Z = 60.1$ . This value has been used as a standard for hydrocarbon solvents by Kosower.<sup>90</sup>

are similarly oriented. Thus, the ground state for 4-methylpyridine-iodoborane must resemble that of the organic analog. In the ground state, the dipole of the ion pair is perpendicular to the plane of the pyridine ring. The iodide ion of the 4-methylpyridine-iodoborane ion pair must lie above the centroid of positive charge (the boron and nitrogen atoms) with the dihedral angle ( $\alpha$ ) in Figure 58 very close to  $90^\circ$ . A conformation with a dihedral angle far from  $90^\circ$  would have a dipole nonperpendicular to the plane of the ring. This conclusion concurs with the conformational analysis of pyridine-iodoboranes presented in an earlier section of the Discussion regarding exchange equilibria and strain phenomena in ortho alkyl-substituted pyridine-iodoboranes.

The substitution of a chlorine atom for a methyl group at the para position of the pyridine ring is also consistent with the charge transfer assignment. In the ground state of the complex, the pyridine moiety is essentially a pyridinium ion, while in the excited state it is primarily a pyridinyl radical. Electron-donating groups are far more effective in stabilizing a carbenium ion species than a free radical species. Electron-donating substituents decrease the electron affinity of the ground state pyridinium ion, stabilizing the ground state without making a corresponding change in the energy of the excited state ring. Electron-withdrawing substituents on the pyridine ring increase its electron affinity, and thus decrease the energy required to reduce it in the

charge transfer transition. The change in  $\lambda_{\text{max}}$  of the charge transfer absorption to lower energy upon chlorine for methyl substitution is consistent with the assignment of this band. The magnitude of the shift (2.5 Kcal/mole) is less than expected by comparison with the effects of hydrogen for methyl substitution at the para position for the N-methylpyridinium iodide system in which a shift of 3.2 Kcal/mole was observed.<sup>90</sup> The discrepancy might reflect that the centroid of positive charge lies further from the ring (close to boron) for the pyridine-iodoborane compounds than for the N-methylpyridinium iodides.

One other feature of the ultraviolet spectrum of 4-chloropyridine-iodoborane supports the assignment of the charge transfer transition. Below 250 nm the spectrum exhibits stronger absorption than that of the corresponding pyridine-borane with a maximum enhancement at approximately 238 nm. Kosower observed a second charge transfer band in the spectra of several substituted N-methylpyridinium iodides.<sup>91</sup> The observation of two charge transfer bands was attributed to the formation of a nearly free iodine atom in the excited state of the complex. The charge transfer transition could result in the production of an iodine atom in either its  $^2P_{3/2}$  ground state or in the  $^2P_{1/2}$  excited state. The energy difference between these states for the free iodine atom is 21.7 Kcal/mole. Since the lower energy charge transfer band appears at 292 nm for 4-chloropyridine-iodoborane

in methylene chloride, a second charge transfer band is expected near 238 nm corresponding to an absorption with a transitional energy 22 Kcal/mole larger. The assignment of the absorption near 238 nm in the spectrum of 4-chloropyridine-iodoborane as a second charge transfer band is somewhat tenuous since other transitions occur in this region. However, solvent and substituent effects on the absorption qualitatively support this analysis.

Thus, it is concluded that pyridine-iodoboranes can exist as tight ion pairs\* in solvents of low polarity with the iodide ion residing above the boron-nitrogen bonding region. This model is well suited for the interpretation of the steric and electronic properties of the Lewis acid,  $\text{BH}_2\text{I}$ , discussed in an earlier section of the Discussion. It was concluded that, in these adducts,  $\text{BH}_2\text{I}$  is sterically similar to  $\text{BH}_3$  despite the larger size of the iodine compared to the hydrogen. It was suggested that the iodine moiety occupies a position above the plane of the pyridine ring (position Y in Figure 58), where steric interactions with ortho alkyl groups are minimal, effectively decreasing the size of the acid portion of the molecule. The same model is proposed independently here to explain charge transfer phenomena of pyridine-iodoboranes.

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\* Trimethylamine-iodoborane may also exist as a tight ion pair, although a charge transfer analysis of this species was not feasible due to the lack of an acceptor moiety within the molecule with an electron affinity sufficient to provide transitions at a working wavelength.

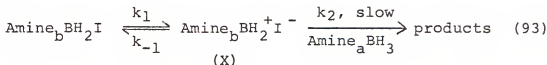
The ion pair model also accommodates the conclusion that, as an acceptor,  $\text{BH}_2\text{I}$  is more sensitive to changes in the base strength of the pyridine donor than is  $\text{BH}_3$ . It was postulated that the greater sensitivity of  $\text{BH}_2\text{I}$  to changes in the electronic properties of the donor could be attributed to more positive charge and/or a more contracted acceptor orbital on the boron atom of this acid compared to  $\text{BH}_3$ . Indeed, the ion pair model requires that these differences exist, since the boron atom of the pyridine-iodoborane is expected to bear a large portion of the net positive charge on the cationic portion of the ion pair.

The ion pair model for amine-iodoboranes is of central importance to the consideration of the cyclic four-center transition state of the  $\text{S}_{\text{F}}$  mechanism. The boron atom of the amine-iodoborane ion pair would have a vacant orbital available for the initiation of the concerted four-center exchange process as described by Lockhart.<sup>1</sup> Further, Herschbach has concluded on the basis of molecular beam studies that, although concerted four-center exchange cannot occur between two covalently bonded molecules, facile four-center exchange is possible between an ion pair and a covalent molecule.<sup>92</sup> The activation energy for exchange can be quite low as long as there is a large disparity of charge between the two atoms of the exchanging bond of one of the reacting species. The boron-iodine bond of the amine-iodoborane ion pair meets this requirement. Facile hydrogen-iodine exchange between the ion



pair and the covalent boron-hydrogen bond of the amine-iodoborane is expected. The iodide ion would remain near the center of positive charge in the transition state (Figure 59) and would migrate from boron atom b to boron atom a as hydride is transferred in the opposite direction.

It is important to recognize the distinction between an intimate ion pair and dissociated ions with respect to kinetic parameters. As mentioned previously, the rate law for an exchange process initiated by predissociation of the boron-iodine bond to the free ions (reaction sequence 75) can exhibit concentration dependence on the amine-borane only if preionization<sup>-</sup> is rapid relative to hydride transfer. In this case, the rate law must express common ion rate depression due to externally added iodide ion (rate law 77). Although a mechanism initiated by predissociation of the amine-iodoborane to the free ions provides the required unsaturation at boron atom b, it does not concur with the observed rate law. By contrast, a reaction sequence proceeding via an intimate ion pair (X) as an intermediate complies with both the unsaturation requirement and the experimental rate law.



The reverse of the ionization step is the return of the intimate ion pair to the covalently bonded molecules (internal return). The three-coordinate boronium cation undergoes in-

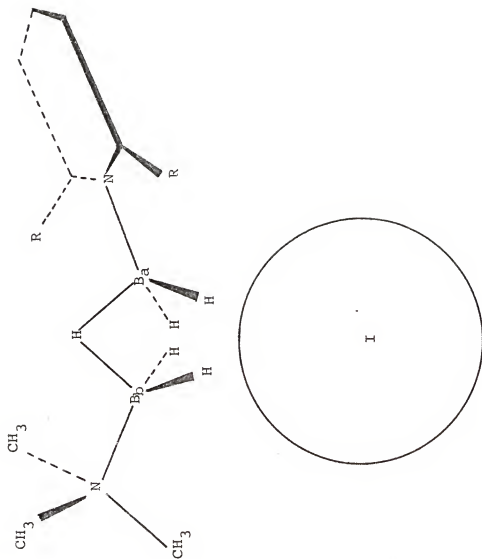


Figure 59.  $S_F$  transition state for the hydrogen-iodine exchange reaction between a substituted pyridine-borane and trimethylamine-iodoborane.

ternal return with its own iodide ion.<sup>85</sup> This particular iodide ion is still closely associated with the cation and is preferentially recaptured. Thus, internal return is not affected by externally added iodide ion and no common ion rate depression appears in the theoretical rate law

$$\text{rate} = k_2 \frac{k_1}{k_{-1}} [\text{Amine}_a \text{BH}_3] [\text{Amine}_b \text{BH}_2 \text{I}] \quad (94)$$

consistent with the experimental rate law. The rate-determining step is the attack of the nucleophilic amine-borane on the ion pair. Backside attack would have all the characteristics of an  $\text{SN}_2$  mechanism, and would be indistinguishable from it in this system,\* whereas frontside attack would initiate the cyclic  $\text{S}_\text{F}$  process.

The effects of altering the halogen atom of the amine-haloborane on the rate of the exchange are consistent with both the  $\text{SN}_2$  and  $\text{S}_\text{F}$  mechanisms. The rate of exchange increases sharply progressing from chlorine to iodine as the halogen on boron. This trend reflects the relative leaving group abilities of the halide ions expected on the basis of bond strengths to boron, basicity, and polarizability, as well as known ease of displacement by other nucleophiles.<sup>48</sup> The effects of changing the halogen might be felt in the position of the ionization preequilibrium, or on the rate of hydride.

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\* Snee and coworkers have demonstrated the intermediacy of the intimate ion pair in the solvolysis reactions of 2-octyl-sulfonates.<sup>86,87</sup>

transfer.

A slower rate for a lighter halogen may be a consequence of a lower equilibrium concentration of the ion pair, decreasing the  $K_{eq}$  of intimate ion pair formation and, thus, the rate of exchange. Alternatively, it may be that the ion pair is held more tightly for a lighter halogen, due to a stronger coulombic attraction between the boronium cation and a smaller, less diffuse halide ion. A tighter ion pair would exhibit less unsaturation at boron, and a slower rate of nucleophilic attack by the amine-borane is expected. For the  $S_F$  mechanism, the rate of this step might also depend on the polarizability of the exchanging halide ion. A large, polarizable anion is better suited for synchronous transfer from one boron atom to the other as the distribution of positive charge shifts in the transition state.

On the surface, neither the  $SN_2$  or  $S_F$  mechanism for hydrogen-halogen exchange appear to comply with the insensitivity of reaction 34 to substitution of deuterium for hydrogen on boron (Table 5). In each of these reaction schemes, a boron-hydrogen bond of the amine-borane is broken in the rate-determining step, so that a primary deuterium isotope effect might be expected. The maximum ratio expected for the relative rates of exchange ( $k_H/k_D$ ) at 35°C is approximately 4.4 based on the complete loss of ground state zero point energy differences in the transition state as determined from infrared stretching frequencies for amine-boranes.<sup>93</sup>

An even larger ratio is expected if the effects of the mass difference of hydrogen and deuterium on the rate of passage over the potential energy barrier (mass factor) is considered. Nevertheless, the absence of a large deuterium isotope effect does not preclude the possible cleavage of the boron-hydrogen bond in the rate-determining step. The results of isotopic substitution on boron suggest that the boron-hydrogen stretching frequency is not altered in the transition state, indicative of a nonlinear activated complex in which hydride is transferred along a reaction coordinate not closely related to the boron-hydrogen stretching vibration of the amine-borane. A triangular arrangement of the three atoms involved in the bridge bond would be required. A bonding arrangement of this type is known to be attainable as evidenced by the structure of diborane which has a boron-hydrogen-boron bond angle of  $83^\circ$ .<sup>94</sup> Hawthorne has postulated a similar configuration for the transition state in the solvolysis reactions of substituted pyridine-diphenylboranes in aqueous acetonitrile to account for the small isotope effect of deuterium for hydrogen substitution on boron.<sup>95</sup> A nonlinear arrangement of the boron-hydrogen-boron bond in the transition state is expected to alter a boron-hydrogen bending frequency of the amine-borane. Since bending frequencies are smaller than the corresponding stretching frequencies, a smaller maximum isotope effect is expected for a nonlinear transition state.

Wiberg has concluded that a reaction which displays a deuterium isotope effect less than the calculated maximum should be considered a three-center process in which the new bond to hydrogen is formed as the old bond is broken.<sup>96</sup> In this case, the difference in zero point energy in the reactants will be partially cancelled by a difference in zero point energy in the activated complex. If the bonding to hydrogen in the transition state is as strong as that in the reactant, there will be no isotope effect attributable to differences in zero point energy. However, the mass factor would remain, and the minimum deuterium isotope effect of 1.4 would be observed. According to this analysis, a deuterium isotope effect near 1.0 should be considered an inverse isotope effect, indicative of a stronger bond to hydrogen in the transition state than in the ground state. Considering that a boron-hydrogen bridge bond of diborane is stronger than a terminal boron-hydrogen bond by 14 Kcal/mole, a stronger bond to hydrogen in a nonlinear transition state is quite reasonable. Thus, it is concluded that a bridged transition state with a triangular arrangement of the three atoms involved in the bridge is consistent with the experimental data. The  $SN_2$  and  $S_F$  mechanisms are equally adequate for adaptation to this description of the activated complex.

Likewise, the insensitivity of the rate of hydrogen-iodine exchange between substituted pyridine-boranes and trimethylamine-iodoborane to changes in the steric properties

of the pyridine donor (Table 6) can be accommodated by either of the bimolecular mechanisms under consideration. The examination of molecular models\* suggests transition states for each pathway in which the two pairs of nonbridging hydrogen atoms on boron are cis to one another with respect to the boron-boron axis (Figures 59 and 60). In this conformation, the bulky methyl groups of trimethylamine-borane are far from the ortho positions of the incoming pyridine ring. No steric interactions between alkyl groups occurs in the transition state even for the bulky ortho-t-butyl group, although boron-nitrogen bond rotations may be restricted. The transition states for the two bimolecular pathways are nearly identical sterically with respect to these frontstrain considerations. In fact, the only significant differences in the geometries of the two activated complexes in Figures 59 and 60 are differences in the hybridization around boron atom b, and in the position of the iodine moiety. In the  $SN_2$  transition state, boron atom b is approximately  $sp^2$ -hybridized with a nitrogen-boron-bridge-hydrogen bond angle of about  $90^\circ$ . In the  $S_F$  transition state, boron atom b is expected to be  $sp^3$ -hybridized with a nitrogen-boron-bridge-hydrogen bond angle of about  $109^\circ$ . Of more importance, the iodide ion exits from the backside of boron atom b in the  $SN_2$  mechanism,

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\* In these models, the boron-hydrogen-boron bridge bond was patterned after that of diborane with a bond angle of  $83^\circ$  and a bond distance of  $1.33 \text{ \AA}$ ,<sup>94</sup> although a larger bond angle might be expected for a singly bridged structure.

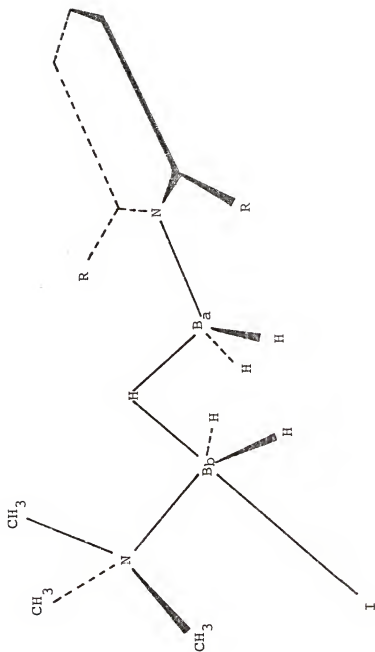


Figure 60.  $S_N2$  transition state for the hydrogen-iodine exchange reaction between a substituted pyridine-borane and trimethylamine-iodoborane.



whereas in the  $S_F$  transition state it remains in the vicinity of the bridging boron atoms. The migration of the iodide ion from boron atom b to boron atom a in the  $S_F$  transition state will not be hindered by bulky ortho ring substituents as long as the dihedral angle between the plane of the pyridine ring and the plane defined by boron atom a, the pyridine nitrogen atom, and the bridging hydrogen atom is near  $90^\circ$ . (For clarification, see Figure 58 with the bridging hydrogen atom as the Y-group). In this configuration, the pyridine-boryl group is in the proper orientation for formation of the incipient pyridine-iodoborane with a structure as described previously with the iodine moiety residing above the aromatic ring.

Further, a highly negative activation entropy is consistent with either of the bimolecular mechanisms, considering the restricted rotations of boron-hydrogen and boron-nitrogen bonds. The highly structured cyclic transition state of the  $S_F$  mechanism is particularly acceptable in this respect.

The effects of altering the electronic properties of the pyridine donor of the pyridine-borane on the rate of hydrogen-iodine exchange are presented in Table 6 ( $k_2$ ). The rate of exchange increases as the electron-donating ability of the para substituent increases, for donors with similar steric requirements. This trend suggests that the boron atom of the amine-borane is electron-deficient in the transition state.

However, the observed substituent effect is quite small with the rate of the 4-methyl derivative only 1.67 times that of the 4-chloro compound. Hawthorne observed comparable substituent effects in the solvolysis reactions of pyridine adducts of di(para-substituted phenyl)boranes in aqueous acetonitrile.<sup>95</sup> It was concluded that the small substituent effects indicated an only slightly electron-deficient boron atom in the transition state. Likewise, it is proposed here that the small substituent effect observed for reaction 52 suggests that boron atom a is only slightly electron-deficient in the activated complex leading to hydrogen-iodine exchange.

The development of only a small quantity of positive charge at boron atom a in the transition state could arise in two ways. One explanation is that very little electron density has been withdrawn from the bond between boron atom a and the exchanging hydrogen atom in the transition state - i.e. very little bridge bond formation to boron atom b occurs in the transition state - a contradiction of previous conclusions. A second, more tenable rationale is that there is a nucleophilic attack by iodide ion on boron atom a concurrent with the loss of hydride ion from that center in the transition state. Thus, the positive charge being generated at boron atom a is nearly neutralized by the approach of the negative iodide ion.

Hawthorne proposed a concerted nucleophilic attack on

boron by solvent simultaneous with electrophilic attack on the boron-hydrogen bond to account for the small substituent effects on the pyridine-diphenylborane solvolysis reactions.<sup>95</sup> Similarly, concurrent nucleophilic and electrophilic attack at boron atom a are proposed here for the hydrogen-iodine exchange reaction. The processes must be concerted, necessitating frontside displacement of iodide ion from the amine-iodoborane. In the  $SN_2$  process, the displaced iodide ion leaves the reaction center from the opposite side of the incoming nucleophilic boron-hydrogen bond, and consequently cannot provide concurrent charge compensation at boron atom a. In the  $S_F$  transition state, the displaced iodide ion migrates toward boron atom a and away from boron atom b by about the same extent. Apparently, the transfer of iodide is not quite as complete as the transfer of hydride in the transition state, since substituent effects suggest the development of a small amount of positive charge at boron atom a. As positive charge is developed at boron atom a by hydride loss, the exchanging iodide ion migrates toward that center. A large, polarizable halide ion such as iodide is well suited for synchronous migration as the center of positive charge changes. A slower rate of exchange for amine-bromoboranes and amine-chloroboranes may reflect inferior migratory aptitudes for the smaller halide ions.

Additional support for the  $S_F$  mechanism as compared to the  $SN_2$  mechanism is provided by the effects of a change in

the polarity of the reaction medium on the rate of reaction 32. The rate of the reaction is essentially unaffected by changes in the ionic strength of the medium (Table 4). In the  $SN_2$  mechanism, it is expected that there is a separation of charge in the transition state as the iodide ion migrates from the cationic portion of the activated complex. Consequently, the reaction rate should increase as polarity of the medium increases. By contrast, in the  $S_F$  mechanism the iodide ion never leaves the vicinity of the cation in the transition state, and reaction rate should be insensitive to changes in solvent polarity.

The remarkable difference in the rate of hydrogen-iodine exchange between 4-methylpyridine-borane and 4-methylpyridine-iodoborane as compared to that for exchange between 4-methylpyridine-borane and trimethylamine-iodoborane warrants some discussion. The second order rate constant for exchange is approximately  $10^5$  times greater for the pyridine-iodoborane (reaction 64) than for trimethylamine-iodoborane (reaction 36). The difference in reaction rates parallels that observed for the organic homomorphs, para-methylbenzyl iodide and neopentyl iodide, in  $SN_2$  displacements.<sup>97</sup> Nainan and Ryschkewitsch have also noted a greater reactivity for pyridine-iodoborane than trimethylamine-iodoborane toward nucleophilic displacement of iodide with pyridine donors, especially when the displacing donor has a large steric requirement.<sup>98</sup> There is no obvious steric interaction in either of the bi-

molecular transition states (Figures 59 and 60) for hydrogen-iodine exchange that would account for the observed difference in reactivity of trimethylamine-iodoborane and 4-methylpyridine-iodoborane. Thus, the difference in reactivity appears to be electronic in origin.

Resonance stabilization of a trigonal boron cation might be advanced as a rationale for the greater reactivity of 4-methylpyridine-iodoborane vs. trimethylamine-iodoborane toward hydrogen-iodine exchange with 4-methylpyridine-borane. Analogs of the trigonal boron cation,  $\text{Amine}_b\text{BH}_2^+$ , that constitutes the positive portion of the intimate ion pair derived from the amine-iodoborane, have been proposed as intermediates in the solvolysis reactions of amine-trichloroboranes in aqueous ethanol,<sup>99</sup> and in the reaction of 4-methylpyridine-trichloroborane with aluminum trichloride.<sup>100</sup> Heaton and Riley attributed the more rapid solvolysis of 4-methylpyridine-trichloroborane vs. trimethylamine-trichloroborane to resonance stabilization of the planar three-coordinate  $\text{Amine}_b\text{-Cl}_2^+$  cation for the aromatic donor. No resonance stabilized cationic transition state is possible for the trimethylamine species. Further, the order of reactivity of organic halides toward hydride abstraction from trimethylamine-borane parallels directly the tendency of the halocarbons to form carbonium ions.<sup>77,101</sup> Substituents on carbon capable of resonance stabilization of the carbonium ion accelerate the rate of hydride abstraction.

Resonance stabilization of the trigonal cation derived from a pyridine-iodoborane would require that the cation have a planar structure with  $sp^2$ -hybridization at boron. However, the  $^{11}\text{B}$  nmr chemical shift of 4-methylpyridine-iodoborane in methylene chloride solution suggests that the trigonal boronium cation is not planar, and that the ion pair is tightly coordinated. The chemical shift of 4-methylpyridine-iodoborane is virtually the same as that of 4-methylpyridine-borane (ca + 30 to + 31 ppm). A large negative chemical shift is expected for the boron atom of a trigonal planar species, particularly if it is positively charged.<sup>100</sup> Thus, the trigonal boron cation of the ion pair does not appear to be planar, and the greater reactivity of aromatic amine adducts of  $\text{BH}_2\text{I}$  cannot be attributed to resonance stabilization of the boronium ion. Consequently, the source of the greater reactivity of pyridine-iodoboranes as compared to trimethylamine-iodoboranes is not immediately apparent.

The rate of hydrogen-iodine exchange between the  $\text{BH}_3$  and  $\text{BH}_2\text{I}$  adducts of a given pyridine donor is relatively unresponsive to changes in the base strength of the donor. This observation can be interpreted in terms of the data presented in Table 6 for the rates of exchange between a pyridine and a trimethylamine adduct. As the base strength of Amine<sub>a</sub> increases, the rate of exchange increases, and as the base strength of Amine<sub>b</sub> increases, the rate of exchange

decreases. As the base strength of the donor in substituted pyridine-borane/pyridine-iodoborane systems increases, the base strengths of both Amine<sub>a</sub> and Amine<sub>b</sub> must increase. The opposing influences of changing both amines cancel, or nearly cancel each other, and the observed rate of exchange is essentially constant for pyridine donors of differing base strengths.

The apparent inertness of the 4-methylpyridine-trifluoroborane/4-methylpyridine-iodoborane system to ligand-ligand exchange merits some comment. No mixed fluorine-iodine adducts,  $4\text{-CH}_3\text{pyBF}_n\text{I}_{3-n}$  ( $n=1$  or  $2$ ), were observed after 6 hr of reaction at room temperature in methylene chloride (1.0 M concentrations), and 4 hr of reaction in refluxing benzene (0.33 M concentrations). The lack of exchange might be kinetic in origin if the boron trifluoride adduct is unable to achieve the bridged transition state accessible to the borane adduct. However, a bridged activated complex of this type should be obtainable for the fluorine compound. Singly bridged amine $\text{BF}_3 \cdot \text{BF}_3$  adducts have been prepared at low temperatures for pyridine and trimethylamine donors,<sup>81</sup> and the  $\text{B}_2\text{F}_7^-$  ion is a stable species in methylene chloride solution.<sup>102,103</sup> Thus, the absence of mixed fluorine-iodine adducts must be attributed to thermodynamic rather than kinetic phenomena. Benton-Jones observed that the reaction of boron triiodide with 4-methylpyridine-trifluoroborane or trimethylamine-trifluoroborane rapidly pro-

duces mixed adducts, but only in trace quantities due to unfavorable equilibria.<sup>22</sup> It appears that fluorine and iodine do not readily coexist on the same boron atom in these adducts.

Although both of the bimolecular mechanisms under discussion adequately account for most of the experimental data, the  $S_F$  reaction path is preferred since it is better suited to a description of the substituent and solvent effects on the rate of exchange. This preference rests on the soundness of the postulates that in the transition state for hydrogen-iodine exchange, boron atom a is only slightly electron-deficient, that the  $SN_2$  mechanism requires a more electropositive boron atom in the activated complex, and that there is a separation of charge between iodide ion and the bridged cation at the energy maximum of the  $SN_2$  process. Although these hypotheses seem reasonable, there is no absolute proof of their validity presented herein.

Overall, the  $S_F$  mechanism is remarkably suited to the insensitivity of the exchange rate to changes in the electronic properties of the pyridine donors. The reaction may be viewed as the concerted attack of two nucleophiles, the boron-hydrogen bond of the amine-borane and the iodide ion, on the two boron atoms. Electron-donating substituents on boron atom b increase the nucleophilicity of the iodide ion, but simultaneously decrease the electrophilic character of that atom toward nucleophilic attack by the boron-hydrogen bond of the



amine-borane. Likewise, electron-donating substituents on boron atom increase the nucleophilicity of the boron-hydrogen bond, and at the same time decrease the susceptibility of that boron atom to nucleophilic attack by iodide ion. Consequently, any changes in the donor properties of one of the amines will have opposing, and at least partially cancelling influences on the exchange rate.

Integral to the acceptance of the cyclic four-center mechanism is the formulation of the new concept that amine-iodoboranes exist as tight ion pairs. With respect to the ion pair concept, it may not be as important to discuss how much the transition state is constituted ionically or covalently, as it is to realize that however electrovalent the bonds may be, they render the transition state cyclic so that substitution retains configuration. Thus, exchange of hydrogen and iodine between an optically active amine-borane derivative,  $\text{Amine}_a\text{BHX}_2$ , and an optically active amine-iodoborane derivative,  $\text{Amine}_b\text{BHXI}$ , would proceed with retention of configuration at both boron atoms. By contrast,  $\text{S}_\text{N}2$  substitution would yield inversion of configuration at boron atom a, and inversion or racemization at boron atom b.

As boron chemistry is developed, the ion pair model for donor-haloborane complexes might have far-reaching consequences in the elucidation of reaction mechanisms at tetrahedral boron. The cyclic four-center transition state may have more general applicability to nucleophilic attack on

donor-haloborane adducts, and to electrophilic attack on boron-hydrogen bonds by a variety of reagents, particularly for species conducive to bridge bond formation. Thus, the ligand-ligand exchange reactions of amine-haloboranes with free boron trihalides (reaction 5) may proceed via a doubly bridged transition state in a concerted process, rather than through singly-bridged intermediates in a stepwise reaction as is generally assumed. The  $S_F$  mechanism may eventually be integral to the interpretation of substituent and stereochemical phenomena of substitution reactions at tetrahedral boron. Further, the ion pair concept may ultimately bridge the gap between the  $SN_1$  and  $SN_2$  mechanisms of donor-haloboranes in the interpretation of reactions with intermediate characteristics, occupying a position of significance comparable to that the model has achieved in the discussion of the nucleophilic substitution reactions of organic halides.<sup>73,85-88</sup>

#### Donor-Halogen Exchange Reactions

##### Kinetics of Bis(pyridine)boronium Iodide Formation

As part of a mechanistic investigation of the reaction of substituted pyridine-boranes with the corresponding pyridine-iodoboranes to form bis(pyridine)boronium iodides and diborane (reaction 43), a kinetic study of the reaction was undertaken. Rate parameters were sought in an attempt to ascertain if a dissociative or nondissociative process were involved. The reaction is expected to follow a rate law of

the form

$$\text{rate (V)} = \frac{-d[\text{R-pyBH}_3]}{dt} = \frac{d[(\text{R-py})_2\text{BH}_2^+\text{I}^-]}{dt} =$$

$$k[\text{R-pyBH}_3]^q [\text{R-pyBH}_2\text{I}]^r = k(a_o - x)^q (b_o - x)^r \quad (95)$$

where  $a_o$  and  $b_o$  are the initial concentrations of the substituted pyridine-borane and pyridine-iodoborane, respectively;  $x$  is the concentration of each reactant consumed at time  $t$ ;  $q$  and  $r$  are the order of the reaction with respect to the substituted pyridine-borane and pyridine-iodoborane, respectively; and  $k$  is the rate constant. When the initial concentrations of the reactants are equal, the integrated rate expressions for overall first and third order rate dependence are, respectively:<sup>69</sup>

$$k_1 t = \ln \frac{a_o}{a_o - x} \quad (96)$$

and

$$k_3 t = \frac{1}{2} \frac{2a_o x - x^2}{a_o^2 (a_o - x)^2} \quad (97)$$

Equation 61 is the integrated second order rate expression.

For 4-methyl substitution, the progress of the reaction was monitored in benzene at 60.0°C by  $^1\text{H}$  nmr integration. The resulting 4-methylpyridine-borane concentration vs. time data are presented in Table 8. The data were analyzed by the integral graphical and tabular methods.<sup>69</sup> In the tabular method of analysis, concentration and time data were substituted into the integrated rate expressions and values

of  $k_1$ ,  $k_2$ , and  $k_3$  were calculated for each sample. The results, including relative standard deviations (Sr), are presented in Table 8 for each integrated rate expression. Integral graphical plots of the same data are presented in Figures 33 through 35. The least squares slopes of these plots provide values for the respective rate constants. For any of the proposed rate expressions, a narrow range of the 95% confidence limits and an intercept through the origin of the least squares plot, and a low value for the relative standard deviation for the tabular calculations, would be indicative of its applicability to the reaction under study. The results presented in Table 8 and Figures 33 and 35 clearly demonstrate that the first and third order rate expressions are not applicable.

For the second order rate expression, it is notable that although the relative standard deviation is high for the tabular method ( $Sr = 27.4\%$ ), the deviations of the data points from the least squares plot in Figure 34 are relatively small (95% confidence limits = 4.0%). Furthermore, the least squares slope determination of  $k_2$  ( $8.40 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ) is significantly less than the mean value of the tabular method ( $1.06 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ ), even though both rate constants were calculated from the same data. The nature of Figure 34 suggests the presence of a constant determinate error which displaces each data point upward by the same constant amount.<sup>104</sup> The suspected constant error was quantitatively correlated

with a signal appearing at 118 Hz in the  $^1\text{H}$  nmr spectrum of the initial reaction mixture before heating (Figure 53). This resonance was identified as a signal of supersaturated bis(4-methylpyridine)boronium iodide, which had been formed rapidly at room temperature before the reaction mixture was heated to 60.0°C. Thus, the reaction had progressed 6.9% toward the products before heating was initiated at time zero. Consequently, the concentrations of the starting materials at time zero were in actuality less than 0.500 M by 6.9% (0.035 M), and the concentrations of starting materials reacted at time  $t$  were actually less by the same quantity. The effects of such an error on the results of the integral graphical method would appear as a constant upward displacement for each data point. However, the effect on the results of the tabular method, which is a ratio of calculation, would be considerably different (cf the appendix for more detail).

To compensate for the effects of the constant determinate error on the kinetic results, the second order calculations were repeated for initial concentrations of the reactants of  $0.500 - 0.035 = 0.465$  M. This adjustment also corrected the concentration of starting materials reacted at time  $t$  to the proper value relative to time zero. The results of second order calculations by this modified procedure are presented in Table 8 ( $k_2'$ ) and Figure 36. The relative standard deviation ( $S_r = 5.84\%$ ) for the tabular calculations is considerably less than that for the unmodified procedure ( $S_r = 27.4\%$ ). Further, the values of the second order rate

constant calculated by the tabular and integral graphical methods are in good agreement for the modified procedure ( $8.14 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $8.40 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ), but not for the unmodified method ( $1.06 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $8.40 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ). Finally, it is noteworthy that an extrapolation of Figure 36 passes through the origin, whereas an extrapolation of Figure 34 does not.

The results discussed above indicate that the boronium iodide salt is formed at a high initial rate, followed by a much slower rate, adhering to second order kinetics, after approximately 13% reaction. The initial rate of the reaction is high even near room temperature, as illustrated by the unexpectedly rapid attainment of the mixture presented in Figure 53. Similar phenomena were observed for the same reaction in methylene chloride at 25°C. The second order rate constants calculated by the tabular method (Table 9) declined significantly as the extent of reaction increased, whereas the fit of the integral graphical plot was considerably better (Figure 37). As before, the plot is a straight line that does not pass through the origin, suggesting the presence of a constant determinate error displacing each data point upward by the same amount. Again, the results are indicative of a relatively rapid reaction during the initial stages, followed by a slower rate obeying second order kinetics over the remainder of the reaction.

Similar results were observed when the course of the

reaction was followed by the isolation of the boronium iodide precipitate (Table 11 and Figure 38). Again, the relative standard deviation for the tabular calculations of the second order rate constant ( $S_r = 15.1\%$ ) is large compared to the deviations of the data points from the least squares plot (95% confidence limits = 9.1%). Further, the mean value of the second order rate constant calculated by the tabular method ( $k_2 = 2.05 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ ) is significantly greater than that determined from the same data by the graphical method ( $k_2 = 1.54 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ ). Finally, Figure 38 has the same appearance as Figure 34 in that an extrapolation of the least squares plot does not pass through the origin. These similarities suggest that the precipitation procedure is also subject to a constant determinate error which displaced each of the integral graphical data points upward by the same amount. As before, this error is attributed to the formation of a significant amount of the bis(4-methylpyridine)boronium iodide at room temperature before any heating. Although no spectral evidence was available in this case to provide an estimate of the magnitude of the error, it could nevertheless be deduced from the intercept at time zero in Figure 38 as 7.0% reaction before any heating. To compensate for the effects of this constant determinate error on the kinetic results, the second order calculations were repeated for an initial concentration of each reactant equal to 0.093 M, and for the concentration of

starting material reacted at time  $t$  reduced by 0.007 M. The results of second order calculations by this modified procedure are presented in Table 11 and Figure 39 ( $k_2'$ ). Once again, a comparison of the modified and unmodified second order calculations is indicative of a high initial rate of reaction followed by a slower rate that obeys second order kinetics. Thus, it can be concluded that reaction 44 follows an overall second order rate law after approximately 10 to 15% reaction.

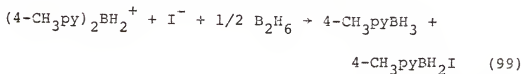
To determine the order of the reaction with respect to each reactant over the same reaction interval, kinetic runs were conducted with unequal initial concentrations of the starting materials. Tabular second order calculations were made for three possible second order rate expressions: first order in each reactant ( $q = r = 1$ ); second order in 4-methylpyridine-borane and zero order in 4-methylpyridine-iodoborane ( $q = 2, r = 0$ ); and zero order in 4-methylpyridine-borane and second order in 4-methylpyridine-iodoborane ( $q = 0, r = 2$ ). The results presented in Table 12 clearly demonstrate that a rate law expressing first order dependence with respect to each reactant is the most appropriate.

$$\text{rate} = k_2[4\text{-CH}_3\text{pyBH}_3][4\text{-CH}_3\text{pyBH}_2\text{I}] \quad (98)$$

However, it must be recognized that this rate law applies only after 10 to 15% reaction has occurred. The initial rate of reaction is considerably faster and obeys a different rate law (vide infra).



A decline in reaction rate as reaction extent increases suggests the possible influence of the reverse reaction (reaction 99) as equilibrium is approached.



This possibility was rejected since a concentrated solution of bis(4-methylpyridine)boronium iodide in methylene chloride under a pressure diborane (ca 22 atm; 100% excess) reacted less than 4% according to equation 99 after 6 days at room temperature. Thus, reaction 99 is much too slow to account for the decline in the second order rate constants for the reverse reaction (Table 9), where a significant decline in the rate constant was observed after 4-5 hr of reaction, even though the concentrations of the boronium iodide and diborane were considerably smaller.

Alternatively, the high initial rate followed by a slower reaction might be attributed to inhibition of the reaction by one of the products. However, since the reaction obeys second order kinetics after the initial period, the inhibitor must be one whose concentration increases during the early stages of the reaction and then becomes constant after saturating the reaction mixture. After achieving saturation, the concentration of the inhibitor would be invariant and the experimental rate law would express no dependence on it. Since diborane is a gas, it would be expected to saturate the reaction mixture after an initial small extent of reaction in noncoordinating solvents such as benzene and

methylene chloride. A similar statement cannot be made with respect to the other product, the bis(4-methylpyridine)-boronium iodide, which is very soluble in methylene chloride. The rate of the reaction was unaffected by externally added bis(4-methylpyridine)boronium iodide, so that no inhibition by this product occurred. Further, in benzene, no correlation was observed between the rate of the reaction and the concentration of supersaturated boronium iodide. The results presented in Figure 40 demonstrate that the reaction is, in fact, inhibited by diborane. The initial rate of reaction for a sample with externally added diborane was approximately one-fourth of that of a control sample with no added diborane.

Thus, it is apparent that the complete rate law for the reaction should express dependence on diborane concentration.

$$\text{rate (V)} = k[4\text{-CH}_3\text{pyBH}_3][4\text{-CH}_3\text{pyBH}_2\text{I}][\text{B}_2\text{H}_6]^s \quad (100)$$

where  $s$ , the order with respect to diborane, must be negative.

Rearranging and taking logarithms, equation 100 becomes

$$\log \frac{V}{[4\text{-CH}_3\text{pyBH}_3]^2} = \log k + s \log [\text{B}_2\text{H}_6] \quad (101)$$

when the initial concentrations of the reactants are equal.

Thus, a plot of  $\log \frac{V}{[4\text{-CH}_3\text{pyBH}_3]^2}$  vs.  $\log [\text{B}_2\text{H}_6]$  will have a

slope of  $s$ , the order of the reaction with respect to diborane.

The instantaneous rate ( $V$ ) of the reaction was monitored at 20.0°C in a mixed solvent system as a function of diborane concentration by combined  $^1\text{H}$  nmr and pressure data. The re-

sults (Table 13 and Figure 43) indicate that the reaction is approximately negative one-half order with respect to diborane ( $s = -0.51$ ), with the complete rate law

$$\text{rate} = k \frac{[4\text{-CH}_3\text{pyBH}_3] [4\text{-CH}_3\text{pyBH}_2\text{I}]}{[\text{B}_2\text{H}_6]^{1/2}} \quad (102)$$

Thus, rate law 98 is a pseudo second order rate law observed in systems in which the concentration of diborane is constant, and  $k_2 = \frac{k}{[\text{B}_2\text{H}_6]^{1/2}}$ . Pseudo second order kinetics are observed in reaction systems open to atmospheric pressure, once the reaction mixture becomes saturated with diborane. The high initial rate of reaction in such systems is easily understood. During the early stages of reaction, the concentration of diborane is low, so its inhibitive influences are less. As the reaction proceeds, the concentration of diborane steadily increases, and consequently the pseudo second order rate constant steadily decreases (cf Tables 8, 9, and 11) until the solution becomes saturated with the gas. Thereafter, pseudo second order kinetics are observed.

Activation parameters were estimated for the reaction from an Arrhenius plot of the pseudo second order rate constants at 23°, 60.0°, and 70.0°C in benzene (Figure 61). An activation enthalpy of 20 Kcal/mole and an activation entropy of -21 cal/mole deg were determined.

#### Mechanism of Bis(pyridine)boronium Iodide Formation

As for ligand-ligand exchange reactions, the reaction of a substituted pyridine-borane with the corresponding pyridine-

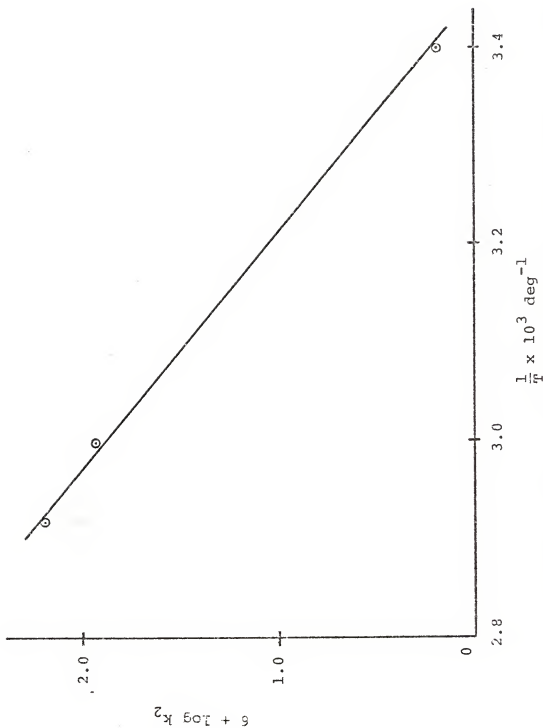


Figure 61. Arrhenius plot for formation of bis(4-methylpyridine)boronium iodide in benzene.

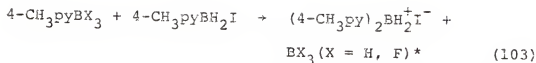
iodoborane to produce diborane and a bis(pyridine)boronium iodide salt might be expected to proceed via a dissociative or a nondissociative pathway. Reaction schemes initiated by homolytic cleavage to form a negatively charged boron fragment (reaction 71) are not viable by reasoning analogous to that discussed for hydrogen-halogen exchange. Heterolytic cleavage of the boron-iodine bond to form a three-coordinate boronium cation and iodide ion can also be eliminated from consideration, since the experimental rate law (equation 102) expresses concentration dependence on the amine-borane without common ion rate depression by iodide ion.

Reaction mechanisms initiated by the heterolytic cleavage of a coordinate boron-nitrogen bond (reaction 68) can also be excluded on kinetic grounds. The coordinate bond enthalpies of borane and iodoborane with 2,6-dimethylpyridine are approximately 2 Kcal/mole less than those with 4-methylpyridine (Table 20). Activation enthalpies for a reaction path initiated by the cleavage of the coordinate bond in the slow step should reflect this difference, and assuming similar Arrhenius preexponential factors, the reaction rate for the 2,6-dimethylpyridine system should be approximately thirty times greater than that of the 4-methylpyridine derivative. To the contrary, the observed rate for 2,6-dimethyl substitution is approximately six times slower than the rate for 4-methylpyridine substitution (Table 14). Further, the estimated activation enthalpy for the 4-methylpyridine system (20 Kcal/mole) is considerably

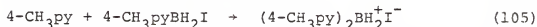
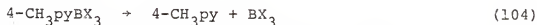
less than the coordinate bond enthalpy of 4-methylpyridine with borane (33 Kcal/mole<sup>63</sup>), which is the lower limit for the activation enthalpy for a reaction initiated by cleavage of the boron-nitrogen bond in 4-methylpyridine-borane.

Additional evidence against predissociation of the boron-nitrogen bond is provided by the solvolysis data of Ryschkewitsch and Birnbaum.<sup>65</sup> Extrapolation of their kinetic data predicts a half-life of approximately 600 hr for the propanolysis of 4-methylpyridine-borane at 25°C. A half-life of 16 hr for reaction 44 was calculated from the initial rate of bis(4-methylpyridine)boronium cation formation in methylene chloride at 25°C (Table 9). Thus, the rate of the reaction under discussion here is considerably greater than that allowable for a process initiated by heterolytic cleavage of the boron-nitrogen bond in the amineborane, despite unfavorable solvation effects in methylene chloride vs. n-propanol. Since iodoborane is a stronger acceptor toward amines than borane, reaction paths initiated by cleavage of the boron-nitrogen bond in the amine-iodoborane can be excluded on similar grounds.

Further support of the exclusion of a reaction mechanism with predissociation of a boron-nitrogen bond in the first step is provided by a comparison of the relative reactivities of 4-methylpyridine-borane and 4-methylpyridine-trifluoroborane toward boronium cation formation with 4-methylpyridine-iodoborane.

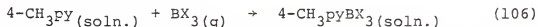


A dissociative process would be initiated by the cleavage of the coordinate boron-nitrogen bond (reaction 104), followed by nucleophilic displacement of iodide ion from the amine-iodoborane by free amine in the second step (reaction 105), resulting in a net reaction with the observed stoichiometry (reaction 103).



The second step in the reaction sequence is independent of the nature of  $4\text{-CH}_3\text{pyBX}_3$ , and thus the relative reactivities of 4-methylpyridine-borane and 4-methylpyridine-trifluoroborane reflect their relative tendencies to undergo the first step in the sequence - cleavage of the dative boron-nitrogen bond.

Figure 62 presents energy level diagrams for coordinate bond formation between dissolved 4-methylpyridine and gaseous monomeric Lewis acid to form solvated adduct (coordination enthalpy =  $\Delta H_{\text{coordination}}$ ).



Fridman<sup>105</sup> and Smith<sup>106</sup> have demonstrated that the reactions of amine donors with boron trifluoride and monomeric borane proceed without activation energy. Thus, there is no energy hump along the reaction coordinate for adduct formation from

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\* In the case of 4-methylpyridine-borane, the free Lewis acid is dimeric ( $1/2\text{B}_2\text{H}_6$ ).

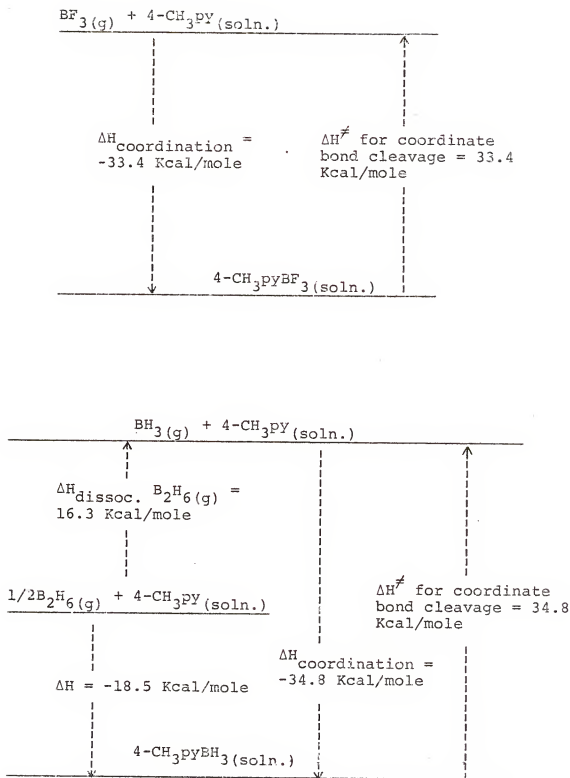


Figure 62. Energy level diagrams for coordinate bond formation and cleavage for the borane and trifluoroborane adducts of 4-methylpyridine in nitrobenzene at 25°C.



the free Lewis acid and Lewis base. The reverse reaction, heterolytic cleavage of the boron-nitrogen bond, proceeds along the same reaction coordinate with an energy maximum identical to that for adduct formation. Thus, the activation enthalpy for the heterolytic cleavage of the boron-nitrogen dative bond is equal in magnitude and opposite in sign to the coordination enthalpy of the adduct. The significance of this analysis is that it is possible to determine the relative activation enthalpies required for the cleavage of the dative bond for two adducts directly from a comparison of their respective coordination enthalpies.

The enthalpy values in Figure 62 refer to nitrobenzene as a solvent and a temperature of 25°C, and all quantities were taken directly or calculated from the thermochemical data of Brown,<sup>63,67</sup> except for the symmetrical dissociation enthalpy of diborane.



Some controversy exists concerning the correct value of this dissociation enthalpy,<sup>107-110</sup> but a lower limit of 32.5 Kcal/mole is compatible with the results of all of these investigations. Thus, a value of 16.3 Kcal/mole will be employed as the dissociation enthalpy of diborane per mole of borane formed. Any higher value only serves to amplify the conclusions of the ensuing discussion.

In order to ascertain the enthalpy of coordination of monomeric borane with 4-methylpyridine, it is necessary to com-

pensate Brown's enthalpy of reaction with diborane (-18.5 Kcal/mole) for the dimerization enthalpy of borane (-16.3 Kcal/mole). Thus, the activation enthalpy ( $\Delta H^\ddagger$ ) for the reverse reaction, cleavage of the coordinate boron-nitrogen bond in 4-methylpyridine-borane, becomes +34.8 Kcal/mole. The coordination enthalpy for the reaction of gaseous boron trifluoride with dissolved 4-methylpyridine is -33.4 Kcal/mole, so that the activation enthalpy for the cleavage of the dative bond in 4-methylpyridine-trifluoroborane is +33.4 Kcal/mole.

Although these activation enthalpies apply to reactions at 25°C, their relative values are not expected to be significantly different at 80°C, the temperature employed herein. Consequently, the activation enthalpy for boron-nitrogen bond cleavage should be less for 4-methylpyridine-trifluoroborane than for 4-methylpyridine-borane, and a faster rate of boronium cation formation would be expected on reaction with 4-methylpyridine-iodoborane for the former species, if a dissociative process occurred. To the contrary, more boronium iodide was isolated for the 4-methylpyridine-borane system (89.2% yield) than for the 4-methylpyridine-trifluoroborane system (14.7% yield) under identical reaction conditions. Thus, the formation of the products via a mechanism initiated by boron-nitrogen bond cleavage can be eliminated as a major pathway.

The foregoing analysis is subject to some qualification since the pertinent reactions examined herein were conducted

in benzene rather than nitrobenzene as a solvent, and since the free boron Lewis acid should be solvated rather than gaseous in the transition state. Solvation effects should be examined with respect to the free Lewis base, the free Lewis acids, and the adducts. Any difference in solvation enthalpy for the donor, 4-methylpyridine, in benzene vs. nitrobenzene would be the same for both the 4-methylpyridine-borane and 4-methylpyridine-trifluoroborane systems and would not influence the relative solvation enthalpies or rates. Both of the dipolar adducts are expected to be solvated less in benzene than in the more polar solvent, nitrobenzene. However, the decrease in activation enthalpy due to lesser solvation in benzene should be greater for the boron trifluoride adduct since it is expected to be more polar than the borane adduct. Thus, inclusion of solvent effects of this type would intensify the validity of the analysis. Although the transition state for the reaction under discussion would surely involve solvated rather than gaseous Lewis acid, solvent effects of this nature would be significant only if borane is solvated considerably more than boron trifluoride. A nonpolar solvent such as benzene is not expected to solvate either Lewis acid significantly. The solvation enthalpy of borane in the donor solvent, nitrobenzene, is only 3.3 Kcal/mole,<sup>63</sup> and a considerably smaller value is probable for the noncoordinating solvent, benzene. Thus, it is highly unlikely that preferential solvation of borane vs. boron trifluoride

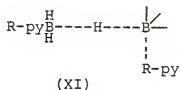
of the magnitude (ca 3.0 kcal/mole) necessary to invalidate the present discussion occurs.

Consequently, a consideration of solvent effects does not alter the conclusion that the boronium iodide is not formed by predissociation of a boron-nitrogen bond as a major reaction path. Only a much higher activation entropy for the 4-methylpyridine-trifluoroborane system vs. the 4-methylpyridine-borane system could affect this analysis.

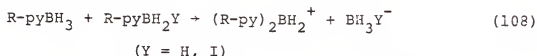
Consequently, it is apparent that the reaction proceeds via a bimolecular collision in the transition state. Boron-nitrogen bond cleavage must be synchronous with bond formation to the same boron atom. Simultaneous bond cleavage and formation are consistent with an activation enthalpy less than the enthalpy of the coordinate bond. Hawthorne has observed activation enthalpies less than the coordinate bond enthalpies of amine-borane adducts when the amine is displaced by a second donor molecule via  $SN_2$  attack.<sup>111</sup>

In the current study, nucleophilic displacement of an amine donor by the iodide ion of a dissociated ion pair can be excluded from consideration since no rate depression was observed with externally added iodide ion. Thus, the most powerful available nucleophile in the reaction system is the boron-hydrogen bond of the pyridine-borane. The boron-hydrogen bonds of an amine-haloborane are less reactive toward electrophiles than those of the corresponding amine-borane.<sup>11</sup> The relative propensities toward boronium cation formation of

a mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane vs. 4-methylpyridine-iodoborane alone can be understood in these terms. Under conditions which resulted in 90% boronium iodide formation for the mixture, the amine-iodoborane system produced less than 3% of the salt. The boron-hydrogen bonds of the amine-borane are more nucleophilic than those of an amine-iodoborane, and therefore, are better suited for nucleophilic displacement of a donor molecule from an adduct.



A transition state of this type might be formed by the reaction of two molecules of the pyridine-borane or one each of the pyridine-borane and the pyridine-iodoborane. In either event, the displacement of the neutral pyridine donor from boron by the hydride moiety from the boron-hydrogen bond of the pyridine-borane molecule would result in the formation of a borohydride type anion as the counterion of the boronium cation.



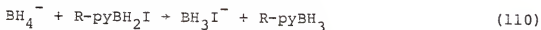
In either event, further reaction would produce the boronium iodide and diborane. The iodoborohydride anion that would result from the reaction of one molecule each of the pyridine-borane and the pyridine-iodoborane is expected to be unstable

with respect to decomposition to diborane and iodide ion.



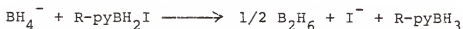
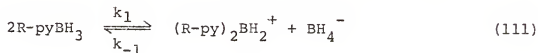
The iodoborohydride anion has never been isolated, presumably due to the instability with respect to the above decomposition reaction. Indeed, diborane and iodide ion are the observed products from the reaction of iodine and borohydride ion, although iodoborohydride anion is expected to be the initial reaction product.<sup>112</sup>

Likewise, the borohydride anion could undergo subsequent reaction to form diborane, although not via simple decomposition as for the iodoborohydride anion. The borohydride anion is considerably more stable to decomposition presumably due to the absence of an easily displaced anion on boron. However, borohydride ion might react with the pyridine-iodoborane moiety that is also present to form the observed products. Considering the reactivity of pyridine-iodoboranes toward the boron-hydrogen bonds of amine-boranes (hydrogen-iodine exchange), it is quite reasonable to expect that the superior hydride donor, borohydride ion, should be very reactive toward a pyridine-iodoborane molecule.



Subsequent decomposition of the iodoborohydride anion would form the observed products. Indeed, 4-chloropyridine-borane and diborane were observed as products from the reaction of borohydride ion and 4-chloropyridine-iodoborane. Thus, the net reaction of two molecules of the pyridine-borane to pro-

duce bis(pyridine)boronium borohydride as an intermediate followed by subsequent reaction with the pyridine-iodoborane is consistent with the observed stoichiometry (reaction 43).



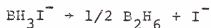
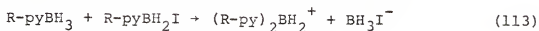
However, such a reaction path is incompatible with the experimental rate law (equation 102). In order to exhibit rate dependence with respect to the pyridine-iodoborane, the second step of the process must be rate-determining. Based on a steady state treatment of the intermediate borohydride ion, the rate law for such a mechanism is

$$\text{rate} = \frac{k_1 k_2 [\text{R-pyBH}_3]^2 [\text{R-pyBH}_2\text{I}]}{k_2 [\text{R-pyBH}_2\text{I}] + k_{-1} [(\text{R-py})_2\text{BH}_2^+]} \quad (112)$$

Consequently, to comply with the observed first order rate dependence with respect to the pyridine-iodoborane, the rate law would have to be second order with respect to the pyridine-borane with inhibition by the boronium cation. Neither of these conditions is consistent with the observed rate law which is first order with respect to the pyridine-borane and exhibits no dependence on the concentration of the boronium cation.

Thus, mechanisms initiated by the reaction of two molecules of the pyridine-borane can be eliminated from discussion. Instead, the pyridine-iodoborane molecule must be the

substrate that is subjected to nucleophilic attack by the boron-hydrogen bond of the pyridine-iodoborane.



A reaction sequence of this type is consistent with the observed first order rate dependence with respect to each reactant. An  $\text{S}_{\text{N}}2$  type displacement rather than a cyclic concerted process ( $\text{S}_{\text{F}}$ ) is favored for the first step of the reaction. The transition state for  $\text{S}_{\text{F}}$  mechanism would be similar to that proposed for hydrogen-halogen exchange with the iodide ion replaced by a pyridine molecule in Figure 59. Unlike the iodide ion, however, the pyridine molecule would have to enter into three-center covalent bridge-bonding in the transition state. No precedent exists for this bonding arrangement. Further, changes in the steric requirements of the exchanging pyridine molecule should markedly influence the rate of reaction due to its proximity to the reaction center. To the contrary, the rates of reaction are nearly identical for 4-methyl and 2-methyl substitution (Table 14). In addition, a concerted reaction which does not involve a free pyridine molecule in the process, is incompatible with the inhibitive effects of diborane on the reaction rate (vide infra).

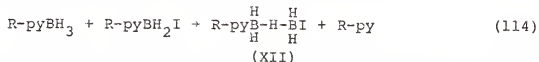
The inhibitive influence of diborane on the rate of the cation-producing reaction could be interpreted in one of three general ways. The first of these is that diborane de-



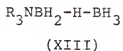
creases the reactivity of a starting material via complexation with it. For instance, diborane could coordinate with the pyridine-borane molecule to form the one to one complex  $R\text{-pyBH}_3\cdot\text{BH}_3$ , a relatively stable species at  $0^\circ\text{C}$ .<sup>81</sup> However, deactivation of a starting material by complexation with diborane can be excluded from further discussion since relatively small concentrations of diborane cause significant declines in the reaction rate. A concentration of dissolved diborane of only approximately 1% that of 4-methylpyridine-borane decreased the rate of the reaction by a factor of more than one-half (Table 13). The second possible mode of rate suppression by diborane would be via a mass action effect on the net reaction, since it is reversible. However, this notion has been excluded from consideration since the reverse reaction (equation 99) is much too slow to account for the observed inhibition, and since inhibition by diborane via this mechanism would also require inhibition by iodide ion, a phenomenon that was not observed experimentally. Thus, it is concluded that diborane exerts its inhibitive influence on the rate via an interaction with a reactive intermediate. The intermediate must be present in low concentration since small concentrations of diborane lead to large reductions in rate.

In contrast to the  $S_F$  mechanism, the  $SN_2$  displacement of a pyridine molecule from the pyridine-iodoborane by a boron-hydrogen bond of the pyridine-borane can be interpreted

readily with respect to inhibition by diborane.



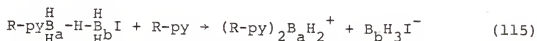
The displaced donor molecule must undergo subsequent reaction to form the observed products. If diborane is also present in the reaction system, it would be expected to complex with the intermediate free amine terminating its progress along the reaction path toward boronium cation production. Uncomplexed amine could react in two ways to form boronium cation. The first of these is the reaction of the displaced amine with bridged intermediate XII. This species would be formed by the displacement of the amine leaving group from the pyridine-iodoborane substrate by a boron-hydrogen-boron bridge bond. This bridged complex is an analog of the borane adduct of pyridine-borane which is stable toward decomposition at 0°C.<sup>81</sup> The same type of bridged intermediate was proposed for the cleavage reactions of diborane with amines.<sup>36</sup>



Further reaction of XIII with free amine formed neutral or charged products depending on the site of attack of the second donor molecule. If the second amine attacked at the same boron atom as the first (asymmetric cleavage), the charged product, the bis(amine)boronium borohydride, resulted. On the other hand, if the second donor molecule attacked at a different boron atom than the first (symmetric cleavage),

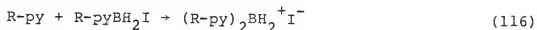
then two molecules of the neutral amine-borane adduct were formed.

Likewise, the bridged intermediate XII is subject to attack at either boron atom by the free pyridine molecule. Attack at boron atom a (asymmetric cleavage) forms the charged products by the displacement of the iodoborohydride anion as a leaving group.

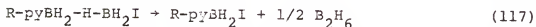


The iodoborohydride anion formed would decompose to diborane and iodide ion, the observed products (reaction 109). Attack at boron atom b (symmetric cleavage) merely regenerates the starting materials in an unproductive reaction sequence.

The second route by which displaced amine could form boronium cation is by the displacement of iodide ion from a second molecule of amine-iodoborane.

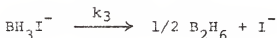
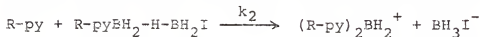
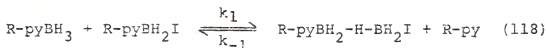


Reactions of this type generally proceed rapidly, and have been exploited for the synthesis of a variety of bis(pyridine)-boronium iodide salts.<sup>49,50</sup> In this event, bridged intermediate XII would decompose to form amine-iodoborane and diborane.

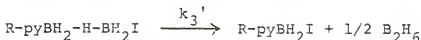
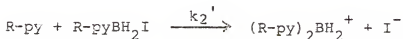
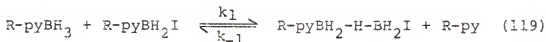


The net results of a reaction sequence initiated by reaction 114 followed by either reaction 115 or 116 comply with the observed stoichiometry. Thus, there are two possible

pathways by which the displaced amine could form the observed products.



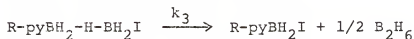
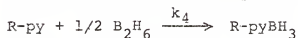
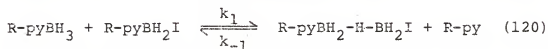
and



In the latter reaction sequence, the displaced amine attacks a molecule of the amine-iodoborane not involved in the formation of the bridged intermediate (XII), whereas in the former mechanism, the displaced amine attacks the bridged species rather than the amine-iodoborane.

In either reaction sequence, the inhibitive influence of diborane is presumably exerted by its ability to complex with the intermediate free amine to form amine-borane, preempting the nucleophilic attack of the amine necessary for boronium cation production. In either of the mechanisms under consideration, the net result of intervention by diborane is to interrupt the reaction sequence leading to boronium iodide production. When accompanied by the collapse of the bridge intermediate (XII) to the amine-iodoborane and diborane,

intervention by diborane has the net effect of regenerating the starting materials in an unproductive reaction sequence.



The progress of the reaction producing boron cation depends on the ability of either the amine-iodoborane or the bridged intermediate to compete with diborane for the free amine. In the latter case, the boron atom originally residing in the amine-borane (boron atom a) would be located in the cation, and in the former case, the boron atom originally residing in the amine-iodoborane (boron atom b) would be located in the cation. Isotopic labelling experiments are of no value in distinguishing between the two possible mechanisms due to the rapid intermolecular hydrogen-iodine exchange reactions characteristic of these systems. However, the two mechanisms can be distinguished in terms of the theoretical rate law that applies to each. Steady state treatments with respect to the bridged species and free amine as a single intermediate lead to the following rate laws for boron cation formation for mechanisms 118 and 119, respectively:

$$\text{rate} = \frac{k_1 k_2 [\text{R-pyBH}_3] [\text{R-pyBH}_2\text{I}]}{k_{-1} + k_2 + k_4 [\text{B}_2\text{H}_6]^{1/2}} \quad (121)$$

$$\text{rate} = \frac{k_1 k_2 [\text{R-pyBH}_3] [\text{R-pyBH}_2\text{I}]^2}{k_{-1} + K_2 [\text{R-pyBH}_2\text{I}] + k_4 [\text{B}_2\text{H}_6]^{1/2}} \quad (122)$$

If the free amine reacts more rapidly with diborane than any of the other possible substrates, then the rate laws become

$$\text{rate} = \frac{k_1 k_2 [\text{R-pyBH}_3] [\text{R-pyBH}_2\text{I}]}{k_4 [\text{B}_2\text{H}_6]^{1/2}} \quad (123)$$

and

$$\text{rate} = \frac{k_1 k_2 [\text{R-pyBH}_3] [\text{R-pyBH}_2\text{I}]^2}{k_4 [\text{B}_2\text{H}_6]^{1/2}} \quad (124)$$

The latter rate law expresses second order rate dependence with respect to the amine-iodoborane, whereas the observed concentration dependence with respect to this reactant is first order. Consequently, mechanism 119 is incompatible with the experimental rate law, and can be rejected. On the other hand, rate law 123 is consistent with the observed rate law (equation 102) with  $k = k_1 k_2 / k_4$ . Thus, mechanism 118, in which a molecule of amine is displaced from the amine-iodoborane by the amine-borane and then cleaves the resulting bridged intermediate asymmetrically, is favored. The displaced amine is expected to reside in the vicinity of the bridged complex during the reaction sequence. After displacement from the backside of boron atom b, the donor must migrate to boron atom a to effect asymmetric cleavage and form the boronium cation. Nucleophilic attack at boron atom b merely regenerates the starting materials. In the absence of diborane, the amine displacement step (reaction

114) is expected to be rate-determining since the boron-nitrogen bond is cleaved in this step. In the presence of diborane, the second step in the sequence must become rate-determining since simple second order kinetics are not observed. Diborane would be expected to drastically reduce the concentration of free amine available for cleavage of the bridged intermediate. Thus, the second step in the sequence is rendered rate-determining by virtue of the low concentration of free amine.

In addition to the rate law, mechanism 118 is also consistent with other experimental data, including the effects of variation in the nature of the amine group coordinated to boron. For example, an 89% yield of the bis(amine)boronium iodide was recovered after 4 hr of refluxing of a benzene solution of 4-methylpyridine-borane and 4-methylpyridine-iodoborane, whereas no boronium iodide salt was produced after 8 days of refluxing of a more concentrated solution of trimethylamine-borane and trimethylamine-iodoborane in benzene. The latter system also failed to yield any boronium iodide when the reactants were heated without solvent in a melt at 85°C for 14 hr. The large difference in reactivity cannot be attributed to a greater boron-nitrogen coordinate bond enthalpy for the aliphatic donor, since the coordination enthalpies of 4-methylpyridine-borane and trimethylamine-borane are nearly identical.<sup>63,64</sup> Thus, a slower rate for the aliphatic system is attributed to steric effects of the

bulky trimethylamine group on the rate of formation of the bridged intermediate or on the rate of asymmetric cleavage of the intermediate with free amine. In the first step of the reaction sequence, in which the bridge bond is formed, the approaching and leaving amine groups are on opposite sides of the transition state bonded to different boron atoms with no severe crowding between them. However, in the asymmetric cleavage step, in which the iodoborohydride leaving group is displaced by the incoming donor, both of the amine groups are on the same side of the activated complex. With trimethylamine as a donor, there is severe crowding between the two amine groups in the transition state, whereas the 4-methylpyridine system is relatively uncrowded. Similarly, Ryschkewitsch and Nainan have observed that iodide ion is more readily displaced from pyridine-iodoborane than from trimethylamine-iodoborane by amine donors.<sup>98</sup>

The results of Shore and Hall also support the notion that the inertness of the trimethylamine system is attributable to steric effects on the second, and not the first, step of the proposed mechanism.<sup>36</sup> When singly bridged borane adducts of amine-boranes (XIII) were reacted with ammonia and some alkyl amines, the relative proportions of symmetric and asymmetric cleavage products varied as the bulk of the amine was changed. With ammonia and methylamine, asymmetric cleavage only was observed, and with the bulky trimethylamine donor symmetric cleavage only was observed. Thus, the tendency



toward boron cation formation in the reaction system studied herein may be controlled to a large degree by the steric requirements of the amine group. Asymmetric cleavage of intermediate XII leads to boronium cation formation, whereas symmetric cleavage regenerates the starting materials in a nonproductive reaction. Bulky amines favor symmetric cleavage, and boronium cation production is hindered, or as in the case of trimethylamine, does not occur at all. Amines with less stringent steric requirements are more likely to yield asymmetric cleavage to form boronium cation. Thus, the effects of ortho methyl substitution on the rate of reaction 43 can be rationalized (Table 14). As ortho hydrogen atoms on the pyridine ring are substituted with methyl groups the rate of the reaction decreases, despite the fact that the coordinate bond between the displaced amine and boron decreases in strength (Table 20). The relative rates in Table 14 reflect a lesser ability of asymmetric cleavage of intermediate XII to compete with symmetric cleavage for the bulkier amine donors. Steric inhibition of asymmetric cleavage leads to a slower rate of boronium cation production for these donors.

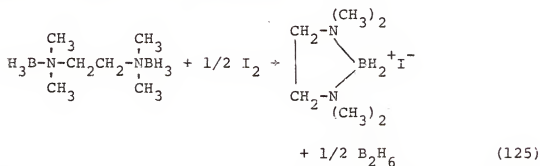
The observed effect of altering the electronic properties of the donor on the rate of reaction 43 is that the rate decreases as the base strength of the amine increases, for donors with similar steric requirements (Table 14). This effect might be exerted in the first step of the reaction

sequence in which the boron-nitrogen bond is cleaved, or in the second step in which the bridge bond is broken. As the base strength of the pyridine donor increases, the strength of the coordinate boron-nitrogen bond of the amine-iodoborane increases (Table 20), and a slower rate of the boron-nitrogen bond cleavage step is expected. A lower value of  $k_1$  for reaction 114 leads to a slower overall rate of boronium cation formation in accord with rate law 123. In the second step of the reaction sequence, positive charge is developing in the vicinity of boron atom as the negative leaving group is displaced. Electron-donating groups on the pyridine ring should stabilize the transition state and increase the rate of reaction. That is, a faster rate is expected for more basic amine donors, in contrast to the observed substituent effects. Thus, it appears that the electronic effect on the overall rate is exerted predominantly in the boron-nitrogen bond cleavage step.

Solvent effects on the rate of reaction 43 are also consistent with mechanism 118. In the rate-determining step, a negative leaving group ( $\text{BH}_3\text{I}^-$ ) is displaced by a neutral nucleophile ( $\text{R-py}$ ). Thus, charge is being developed in the transition state, and the reaction should proceed faster in a more polar solvent.<sup>112</sup> The rate of boron cation production via reaction 43 is in fact greater in methylene chloride ( $k_2 = 3.65 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$  at  $25^\circ\text{C}$ ) than in the less polar solvent benzene ( $k_2 = 2.7 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$  at  $25^\circ\text{C}$  from

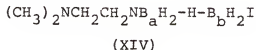
Figure 61).

In sharp contrast to the inertness of the trimethylamine-borane/trimethylamine-iodoborane system toward boronium cation formation reported herein, the iodination of the bis(borane) adduct of tetramethylethylenediamine readily leads to boronium iodide production.<sup>113</sup>



A 93% yield of the iodide salt of the chelated boronium cation was isolated after 2 hr of reaction in refluxing benzene. The greater reactivity of the chelated system may be due in part to a weaker bond between nitrogen and iodoborane. The second base constant of ethylenediamine is less than the first by more than three  $pK_a$  units.<sup>114</sup> Thus, coordination of a diamine nitrogen atom to a Lewis acid should decrease the basicity and consequently the donor strength of the other coordination site toward a second molecule of Lewis acid. However, this factor alone could not account for the dramatic difference in reactivities of the diamine and trimethylamine systems. For example, the rate of reaction 43 for 4-chloro substitution is only about twice that for 4-methyl substitution even though there is a difference in base strength of more than two  $pK_a$  units for the two donors.

Sterically, the diamine system is more encumbered than the trimethylamine system. Thus, it appears that the greater reactivity of the former must be attributed to a conformational effect. Examination of molecular models indicates that it is feasible for the framework formed by the borane boron atom, the two nitrogen atoms, and the two bridging carbon atoms of a monoiodinated intermediate,  $\text{H}_3\text{BN}(\text{CH}_3)_2\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_2\text{BH}_2\text{I}$ , to achieve a conformation very similar to that expected for the chelated product. Once the bond between boron atom b and nitrogen has been cleaved by intramolecular boron-hydrogen bridge formation, a rotation about the bond between boron atom a and nitrogen in the intermediate bridged species (XIV) produces a conformer ideally suited for chelate formation.



The iodoborohydride leaving group and the pendant free amine moiety are on opposite sides of boron atom a in this conformation. Nucleophilic displacement of the iodoborohydride anion by the pendant amine produces chelated boron cation. This asymmetric cleavage step is not subject to the same steric considerations as for the trimethylamine system. In the latter case, there are severe steric repulsions between the methyl groups of the incoming and coordinated trimethylamine moieties. Attack at the boron atom without a coordinated amine group is favored (symmetric cleavage), and no

boronium cation is formed. In the diamine system, instead of a steric repulsion between the two amine groups, there is an attractive force between them - namely, the covalent bonding of the bridging ethylene moiety - which holds the pendant amine in the vicinity of boron atom a, as required for boronium cation formation.

The notion that for reaction 43 the displaced amine attacks the bridged intermediate (XII) rather than a molecule of amine-iodoborane (mechanism 119) is supported by the results found with the diamine system. No linear chain or larger cyclic products were isolated, nor were they believed to be intermediates in the reaction.<sup>113</sup> Products of this type would be formed by the intermolecular attack of a pendant amine group of the bridged intermediate on another molecule of intermediate or starting material. Thus, the chelated product results by the intramolecular displacement of iodoborohydride from boron atom a by the pendant free amine. By analogy, the free amine in reaction mechanism 118 returns to the bridged intermediate. Nucleophilic attack at boron atom a produces boronium cation.

In summary, it appears that four requirements must be met for a system containing an amine adduct of a Lewis acid ( $R_3NBX_3$ ) to form bis(amine)boronium cation under nondissociative conditions.

(1) A substrate must be present with a displaceable amine group. This species may be  $R_3NBX_3$  itself or another amine-

Lewis acid adduct.

(2)  $R_3NBX_3$  must be capable of displacing the amine from a second molecule of adduct via the formation of a B-X-B bridge bond.

(3) The displaced amine group cannot be so bulky as to preclude asymmetric cleavage of the bridged intermediate for steric reasons.

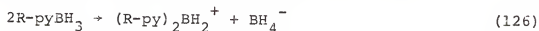
(4) The negatively charged counterion of the boronium cation product must be compatible with it. For example, an anion capable of reducing the boron cation via amine displacement would not be suitable.

A solution of 4-methylpyridine-iodoborane alone is relatively unreactive toward boronium cation formation for failure to comply with the second requirement. The boron-hydrogen bonds of amine-haloboranes are less reactive toward electrophiles than those of the parent amine-boranes.<sup>11</sup> A solution of an amine-iodoborane contains no boron-hydrogen bonds sufficiently nucleophilic to effect amine displacement via bridge bond formation. The solution must also contain an amine-borane for boron cation to be produced.

The trimethylamine-borane/trimethylamine-iodoborane system fails to produce boronium cation for lack of compliance with the third requirement. Bulky amines can form chelated boronium cations, however, when both amines reside in the same molecule (i. e., a diamine).

A solution of a pyridine-borane alone is relatively

stable to boronium cation production due to incompatibility with the fourth requirement. The anion that would be formed as the counterion of the boronium cation by the reaction of a pyridine-borane would be the borohydride anion.

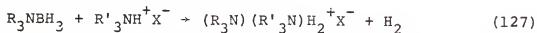


Bis(pyridine)boronium cations can be reduced by borohydride ion in aqueous solution.<sup>115</sup> Thus, although it is expected that the boronium cation is accessible kinetically in a solution of a pyridine-borane, the product is not observed due to unfavorable equilibrium with respect to the neutral adduct.

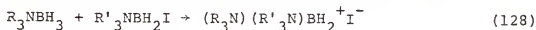
By analogy, one might expect that a solution of a pyridine-borane and a pyridine-iodoborane should not be able to form boronium cation. The iodoborohydride counterion should have reducing properties similar to those of the borohydride anion with respect to the boronium cation. However, there is a notable difference in the stabilities of the two anions. The iodoborohydride anion is believed to be unstable with respect to diborane formation via the loss of iodide ion. As a result, species are formed that are not capable of reducing the boronium cation. Virtually no reduction of the bis(4-methylpyridine)boronium cation occurred on long standing of a solution of the iodide salt under a pressure of diborane. Thus, a mixture of 4-methylpyridine-borane and 4-methylpyridine-iodoborane is well suited for bis(amine)boronium cation formation. The amine-iodoborane

contains a displaceable amine, the amine-borane provides a nucleophile suitable for bridge bond formation, 4-methylpyridine is not sterically encumbered as the free amine, and the iodoborohydride anion is not capable of reducing the boronium cation by virtue of its instability with respect to decomposition.

The reactions of amine-boranes with Lewis acid adducts of amines to form bis(amine)boronium cations are not limited to reactions of the amine-borane with boron Lewis acid adducts. Miller and Muetterties have synthesized bis(amine)boronium cations by the reaction of amine-boranes with ammonium salts at high temperature and pressure.<sup>116</sup>



By this method it is possible to prepare mixed cations with two different amines coordinated to boron. In general, it is expected that the preparation of cations of this type would not be practical by the reaction of the borane adduct of one amine with the iodoborane adduct of another amine.



Hydrogen-iodine exchange between the two starting materials would produce a mixture of two amine-boranes and two amine-iodoboranes. The formation of the mixed cation from the borane adduct of one amine and the iodoborane adduct of the other could be accompanied by the formation of the two unmixed cations by the reactions of the borane and iodoborane



adducts of identical amines. Pure unmixed cation could be prepared if the rate of its formation from amine-borane and amine-iodoborane were significantly greater than the rates for unmixed cation formation, if the hydrogen-iodine exchange reaction were slower than cation formation, or if the hydrogen-iodine exchange equilibrium were favored to a large extent to one side. The latter two conditions have not been observed. The first condition may be responsible for the formation of mixed chelated cations from the reactions of the bis(borane) adducts of asymmetrical diamines with iodine. It appears that in these systems, intramolecular reaction of amine-borane and amine-iodoborane moieties to form boronium iodide salt is considerably faster than intermolecular reaction, since the only products obtained contain just one boron atom per cation. Since intramolecular reaction must lead to the formation of mixed boron cation, this is the only boronium ion produced. Hydrogen-iodine exchange between borane and iodoborane moieties coordinated to unidentical donor sites will not alter the course of the reaction so long as boronium cation formation is an intramolecular process.

The stability of amine-boron Lewis acid adducts in general toward bis(amine)boronium cation formation can be interpreted in terms of the four criteria mentioned previously. Adducts of bulky amines are expected to be stable by virtue of unfavorable competition between symmetric and asymmetric cleavage of the bridged intermediates. Adducts of unencum-

bered amines may or may not be stable to boronium cation formation depending on the Lewis acid. Adducts of borane are stable due to incompatibility of the cation and anion formed. Adducts of iodoborane are stable due to the lack of a ligand on boron suitable for bridge bond formation.

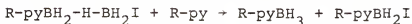
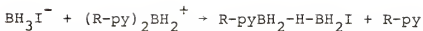
Amine adducts of the boron trihalides might be expected to disproportionate to form boronium cations. Halogens are suitable as bridging ligands as evidenced by the existence of certain  $B_2X_7^-$  anions,<sup>102,103</sup> and by the rapid halogen redistribution reactions of mixtures of two or more boron trihalides.<sup>1,6,8</sup> Further, the tetrahaloborate anion is suitable as a counterion of the boronium cation. Boronium tetrahaloborates have been proposed as reaction products from the disproportionation of a few amine-boron trihalide adducts.<sup>29,30,62</sup> However, the quantities of boronium tetrahaloborate formed were quite small, and in general it can be stated that amine-trihaloborane adducts are stable toward boronium cation formation, particularly when compared to amine-borane/amine-iodoborane systems. The greater stability of the boron trihalide adducts might be attributed to the greater acidity of the Lewis acids (boron trifluoride is an exception). The amine molecule in these adducts is more difficult to displace with the incoming bridge bond due to a stronger coordinate link to the boron Lewis acid.

The stability of amine-boron trifluoride adducts to boronium tetrafluoroborate formation cannot be attributed to

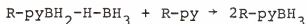
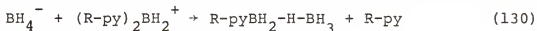
complexation enthalpy since boron trifluoride and borane are comparable in acid strength toward amine donors.<sup>60,67</sup> The stability must be of some other origin, perhaps the inability of the system to form a boron-fluorine-boron bridge bond, or to cleave it asymmetrically. Indeed, 4-methylpyridine-trifluoroborane and 4-methylpyridine-iodoborane do not react via the formation and asymmetric cleavage of a boron-fluorine-boron bridge bond. Asymmetric cleavage of this type would lead to a difluorobis(4-methylpyridine)boronium cation as a product, which was not observed. The dihydrobis(4-methylpyridine)boronium cation that was formed must have resulted from some other mechanism not analogous to reaction scheme 118.

In accord with the principle of microscopic reversibility, the reduction of bis(4-methylpyridine)boronium iodide with diborane (reaction 99), which is the reverse of reaction 43, must proceed via the same intermediates. In this case, the first step in the reaction sequence would be the formation of the iodoborohydride anion from the reaction of diborane and iodide ion. Next the iodoborohydride ion would displace a molecule of donor from the boron cation via bridge bond formation to produce intermediate XII. Finally, symmetric cleavage of the bridged intermediate by the displaced amine yields one molecule each of amine-borane and amine-iodoborane, the observed products.





Likewise, the reduction of bis(pyridine)boronium cations with borohydride anion can be interpreted in terms of a similar mechanism. Amine displacement via bridge bond formation between the anion and cation produces a bridged intermediate analogous to structure XII. Symmetric cleavage yields the observed products, two molecules of amine-borane



Although it is not generally feasible to prepare bis-(pyridine)boronium cations from pyridine-boranes, presumably due to the reducing ability of the borohydride counterion, the synthesis of these cations from pyridine-borane/pyridine-iodoborane mixtures is practical due to the instability of the iodoborohydride anion with respect to diborane. The synthesis is favored both thermodynamically and kinetically by the removal of diborane from the reaction system, since the overall reaction is reversible and since diborane inhibits the cation-producing reaction. An additional driving force for the reaction is the precipitation of the insoluble boronium iodide salt in solvents of low polarity. Thus, the reaction of a solution of a pyridine-borane with one-half of an equivalent of iodine in a nonpolar solvent in an apparatus which allows diborane to escape represents a viable

synthesis for bis(pyridine)boronium cations. This synthetic procedure has also been exploited for the preparation of a variety of chelated boronium cations from aliphatic and aromatic diamine-bis(boranes).<sup>113</sup>

Certain similarities and differences between the boronium cation producing reaction (reaction 43) and the hydrogen-iodine exchange reaction (reaction 52) should be mentioned. In each case, it is proposed that a leaving group is displaced from the amine-iodoborane by the nucleophilic attack of a boron-hydrogen bond of the amine-borane. The bridged species which results is subject to nucleophilic attack at either boron atom by the displaced moiety.\* Attack at the boron atom originally residing in the amine-borane molecule leads to the formation of the products, whereas attack at the boron atom originally residing in the amine-iodoborane molecule regenerates the starting materials.

In the cation-producing reaction the displaced moiety is a pyridine molecule and in the hydrogen-iodine exchange reaction it is the iodide ion. Considering the basicity of each leaving group, it is not surprising that the hydrogen-iodine exchange reactions are more rapid than the boronium cation formation reactions. When the boron-hydrogen bond of an amine-borane attacks a molecule of an amine-iodoborane the better leaving group (iodide ion) is displaced more

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\* In the  $S_F$  mechanism for hydrogen-iodine exchange, the displacement and nucleophilic attack steps are synchronous.

frequently leading to a faster rate for the hydrogen-iodine exchange reaction.

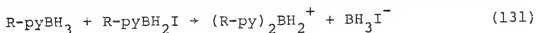
Likewise, the difference in the effect of diborane on the reaction rates of the hydrogen-iodine exchange and cation-producing reactions can be understood in terms of the donor properties of the respective leaving groups from the amine-iodoborane. Pyridine donors form stable complexes with borane, whereas iodide ion does not. Consequently, the cleavage of a bridged intermediate by the nucleophilic attack of a free pyridine molecule will be impaired in the presence of diborane, and cleavage by iodide ion will not. Thus, the cation-producing reaction is inhibited by diborane, and the hydrogen-iodine exchange reaction is not.

The effects of changing the donor properties of the pyridine moiety are also different for the two reactions types. For the cation-producing reaction, reaction rate decreases as the base strength of the donor increases, for amines with similar steric requirements (Table 14). The trend can be attributed to the fact that a boron-nitrogen bond must be broken during the course of the reaction. For hydrogen-iodine exchange (reaction 52) no boron-nitrogen bond is cleaved, and the opposite trend is observed for the influence of base strength on reaction rate ( $k_2$  in Table 6).

The two reaction types also exhibit somewhat different sensitivities to variations in the steric requirements of the pyridine donor. For hydrogen-iodine exchange the rates are

nearly equal for 2-methylpyridine-borane and 2,6-dimethylpyridine-borane, whereas for the cation-producing reaction the rate for the 2-methyl derivative is approximately five times that of the 2,6-dimethyl derivative. The greater sensitivity of the cation-producing reaction to steric factors may reflect the fact that during the course of the reaction sequence an amine molecule must approach a boron atom with another donor already coordinated to it. In the hydrogen-iodine exchange reaction, it is not necessary for two donor molecules to come in close proximity of one another, and steric interactions between them are less significant.

The two reaction types are also different thermodynamically. The hydrogen-iodine exchange reactions have equilibrium constants very near one. Although no equilibrium constants were determined for the cation-producing reaction, it is apparent from the evidence presented herein that reaction toward the boronium iodide and diborane is favored. In the hydrogen-iodine exchange reaction, the numbers and kinds of bonds remain constant as boron-hydrogen and boron-iodine bonds are redistributed between amine-boryl moieties. Thermoneutrality might be expected, and is very nearly observed in all cases studied (Table 20). Before decomposition of the iodoborohydride anion occurs, the cation-producing reaction can also be viewed as an exchange reaction in which boron-nitrogen and boron-iodine bonds are redistributed.



Again, the numbers and kinds of bonds present remain constant and thermoneutrality or near thermoneutrality might be expected. If the only entropy change is the redistribution entropy, then an equilibrium constant close to one is expected. Thus, the conclusion that the reaction is favored toward boronium cation formation must be attributed to the instability of the iodoborohydride anion with respect to diborane formation. The formation of diborane is a driving force available to the cation-producing reaction that is not accessible to the hydrogen-iodine exchange reaction. The removal of the reaction products - diborane as a gas, and the boronium iodide as an insoluble salt in nonpolar solvents - is an additional driving force available to the cation-producing reaction.



## APPENDIX DISCUSSION OF ERRORS

### Equilibrium Constants

The methods used to establish error limits for the concentration terms and ultimately for the values of the hydrogen-iodine exchange equilibrium constants in Table 1 are illustrated below for 4-chloro substitution (reaction 37). Figure 63 presents a 50 Hz sweep width  $^1\text{H}$  nmr spectrum of the reaction mixture obtained after 5 hr at  $35^\circ\text{C}$  for a solution originally containing 1.0 M 4-chloropyridine-borane and 1.0 M trimethylamine-iodoborane in methylene chloride. The chemical shift region shown is approximately from 140 Hz to 190 Hz. The two major resonances, peaks a and c, correspond to the chemical shifts of trimethylamine-borane and trimethylamine-iodoborane, respectively. Peak b is a minor unidentified resonance observed in the reaction mixtures of most of the pyridine derivatives investigated. Region a includes one portion of a broad quartet assigned to protons bonded to the  $^{11}\text{B}$  isotope in trimethylamine-borane.

Using  $^1\text{H}$  nmr spectra of pure trimethylamine-borane and trimethylamine-iodoborane taken under similar conditions as guides, the spectrum of the reaction mixture was manually apportioned into areas attributed to each solute. In Figure 63, the area of the amine-borane is maximized and the area

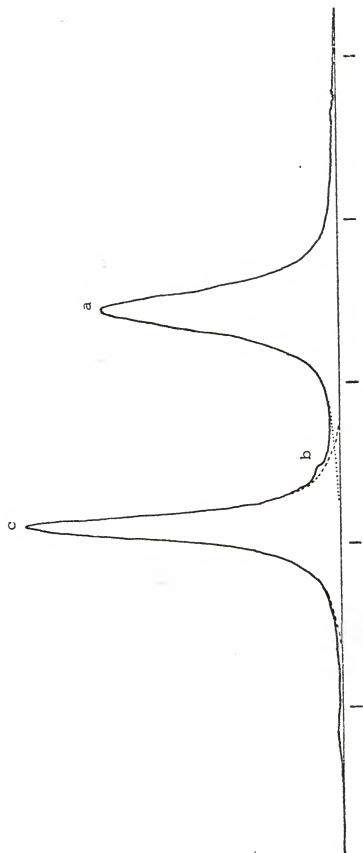


Figure 63. Apportionment of trimethylamine resonances to maximize Keg. Resonance a corresponds to trimethylamine-borane and resonance c to trimethylamine-iodoborane. (50 Hz sweep width).

of the amine-iodoborane is minimized, within reasonable limits, whereas in Figure 64 the converse is true. Each figure was traced three times with a planimeter to determine the relative areas of each region of the spectrum. Trimethylamine-borane areas were multiplied by a factor of 0.937 (equation 12) to eliminate the effects of resonance due to boron-bonded protons. The results, normalized to a total area of trimethylamine resonances of 1.000, are presented in Table 22.

The concentrations presented in Table 1 for the trimethylamine adducts are the arithmetic means with average deviations for the two extreme apportionments of the  $^1\text{H}$  nmr spectrum. The concentration range given in Table 1 for the dissolved bis(4-chloropyridine)boronium iodide salt was determined directly by integration of the aromatic region of a 500 Hz sweep width  $^1\text{H}$  nmr spectrum.

Maximum and minimum values for the equilibrium constant for hydrogen-iodine exchange were calculated from the concentrations in Table 23 and equation 46. The concentrations of the pyridine adducts in Table 23 were calculated from equations 15 - 18. An upper limit for the equilibrium constant was determined from the data derived from Figure 63, where the trimethylamine-borane area was maximized and the trimethylamine-iodoborane area was minimized. Use of this data has the effect of maximizing the ratio  $[(\text{CH}_3)_3\text{NBH}_3]/[(\text{CH}_3)_3\text{NBH}_2\text{I}]$  in the equilibrium expression. In order to

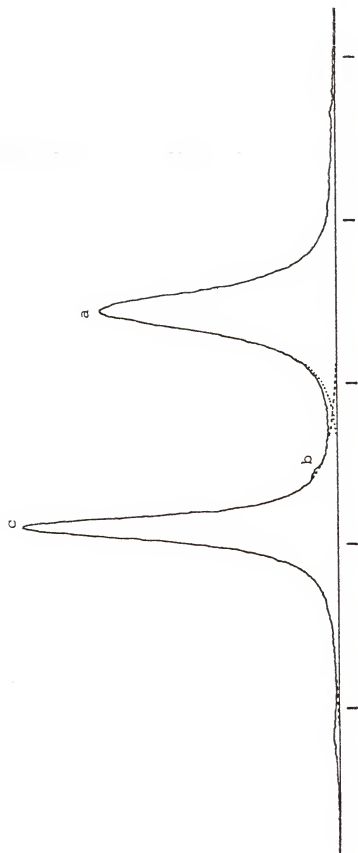


Figure 64. Apportionment of trimethylamine resonances to minimize  $K_{eq}$ . Resonance a corresponds to trimethylamine-borane and resonance c to trimethylamine-iodoborane. (50 Hz sweep width).

Table 22  
Integrated Areas for Figures 63 and 64

	Trial 1	Trial 2	Trial 3	Average
Figure 63 Area a	0.532	0.532	0.528	0.531
Area b	0.001	0.001	0.001	0.001
Area c	0.467	0.467	0.471	0.468
Figure 64 Area a	0.518	0.520	0.524	0.521
Area b	0.001	0.001	0.001	0.001
Area c	0.481	0.479	0.475	0.478

Table 23  
Equilibrium Concentrations for the Maximum and Minimum Values of  $K_{eq}$

$[(CH_3)_3NBH_3]_e$	$[(CH_3)_3NBH_2I]_e$	$[4-ClpyBH_2I]_e$	$[4-ClpyBH_3]_e$	$[(4-Clpy)_2BH_2I^+]_e$	$[164]_e$	$K_{eq}$
0.531 <sup>a</sup>	0.468 <sup>a</sup>	0.379	0.315	0.153	0.001	1.36
0.521 <sup>b</sup>	0.478 <sup>b</sup>	0.376	0.334	0.145	0.001	1.22

<sup>a</sup> From Figure 63

<sup>b</sup> From Figure 64

find upper limit for the equilibrium constant the ratio  $[4\text{-ClpyBH}_2\text{I}]/[4\text{-ClpyBH}_3]$  should also be maximized. To do so, the upper limit for the bis(4-chloropyridine)boronium iodide concentration (0.153 M) was used in calculating the concentrations of the 4-chloropyridine adducts. Finally, the unidentified peak at 164 Hz was assigned as a product of a secondary reaction of trimethylamine-borane rather than trimethylamine-iodoborane. As a result, the equilibrium concentration of 4-chloropyridine-iodoborane was calculated from equation 17, and the equilibrium concentration of 4-chloropyridine-borane was determined by subtracting the concentration of the boronium iodide from that of trimethylamine-iodoborane.

The overall effect of the above procedure was to allow the maximum additive contributions of all the errors under consideration toward an upper limit for the equilibrium constant. By a similar process, a minimum value for the equilibrium constant was determined. The data in Table 23 derived from Figure 64 were used to minimize the ratio  $[(\text{CH}_3)_3\text{NBH}_3]/[(\text{CH}_3)_3\text{NBH}_2\text{I}]$ . To minimize the ratio  $[4\text{-ClpyBH}_2\text{I}]/[4\text{-ClpyBH}_3]$  the lower limit for the bis(4-chloropyridine)boronium cation concentration (0.145 M) was used, and the peak at 164 Hz was assigned to a product of a secondary reaction of trimethylamine-iodoborane. The equilibrium concentration of 4-chloropyridine-borane was calculated from equation 18, and the equilibrium concentration of 4-chloro-

pyridine-iodoborane was determined by subtracting the boron iodide concentration from that of trimethylamine-borane. Thus, the maximum additive effects of all the sources of uncertainty under consideration toward a minimum value of the equilibrium constant were allowed.

The value of the equilibrium constant reported in Table 1 is the arithmetic mean with average deviation for the two extreme values calculated by the methods described above. Similar procedures were employed to obtain ranges for the equilibrium concentrations and equilibrium constants for the other pyridine derivatives in Table 1.

### Rate Constants

#### Hydrogen-Iodine Exchange

The rate constants presented in Tables 4 and 5 were determined from the slopes of least squares plots of the appropriate form of the integrated second order rate equation (equations 60 and 61) vs. time. The confidence limits recorded for the least squares slopes and intercepts correspond to 95 % confidence levels. For each plot there is a 95 % probability that the true slope lies within the confidence interval established by the experimentally derived slope and the confidence limits.<sup>117</sup> In all cases, coefficients of correlation between the dependent and independent variables were in excess of 0.99, indicating that changes in reactant concentration were attributable to reaction time only, and no other variable.<sup>118</sup>



### Bis(pyridine)boronium Cation Formation

Two methods of analysis were employed for the determination of the second order rate constants ( $k_2$ ) for the reaction of 4-methylpyridine-borane and 4-methylpyridine-iodoborane to form the bis(4-methylpyridine)boronium iodide salt (reaction 44). The least squares integral graphical method was employed as described above for hydrogen-iodine exchange. In addition, the tabular method of analysis was used. With the latter procedure, concentration and time data pairs are substituted into the appropriate integrated second order rate equation (equations 60 and 61), and values of the rate constant are calculated for each pair. The relative standard deviation ( $S_r$ ) of the resultant values of the rate constant with respect to the mean is a measure of the precision of the results.

It is noteworthy that for reaction 44 in benzene at 60.0°C, the precision of the least squares slope in Figure 34 as indicated by the narrow 95 % confidence limits, is considerably better than that of the tabular method (Table 8), even though the same data were used for each method. Furthermore, the least squares slope value for  $k_2$  is significantly less than the mean value of the tabular method.

The differences arise from a basic weakness of the tabular method, which is a ratio method of calculation.<sup>104</sup> The tabular second order rate constants are calculated as ratios of concentration terms divided by time.

$$k_2 = \frac{x}{a_o(a_o - x)} / t \quad (132)$$

Ideally, as the reaction proceeds this ratio should remain constant (within the limits of inevitable indeterminate errors). However, if there is a constant determinate error affecting the numerator of this ratio (i.e.  $\frac{x}{a_o(a_o - x)}$ ), the magnitude of the effect on  $k_2$  varies as the magnitude of the numerator and denominator vary. That is, as the reaction proceeds, the calculated values of  $k_2$  reflect not only the inevitable random errors in the variables, but also depend on the constant determinate error, since the magnitude of the effect of that error on the ratio varies. If the constant determinate error makes a positive contribution to the numerator of the ratio, the calculated values of  $k_2$  continually decline as the reaction proceeds, since the relative effect of the error declines as the magnitude of the numerator increases. Such a decline is exactly the behavior exhibited by the tabular values of  $k_2$  in Table 8. Inspection of the calculated values of  $k_2$  in the table gives the erroneous impression that second order kinetics are not observed over the portion of the reaction investigated.

By contrast, the integral graphical method is not subject to the same weakness as the tabular procedure. If there is a constant determinate error in the dependent variable  $Y$  ( $Y = \frac{x}{a_o(a_o - x)}$ ), then all of the data points in the plot are displaced upwards (or downwards) by the same amount. The data points still lie along a straight line intersecting

the ordinate at a point dependent upon the sign and magnitude of the determinate error. The slope of the line, which is equal to  $k_2$ , is not altered by the presence of the constant determinate error. Only the intercept of the plot is altered. The value of the slope ( $k_2$ ) and the precision to which it is measured are the same whether the plot passes through the origin or not. The ratio method on the other hand, assumes that the plot passes through the origin, and the calculated values of  $k_2$  will be imprecise if it does not. Since the value of the slope (and thus  $k_2$ ) is independent of the presence of the constant determinate error, the graphical method of analysis has an advantage over the tabular method. Furthermore, the slope of the plot is nothing more than the change in the dependent variable ( $\frac{x}{a_0(a_0 - x)}$ ) per unit change in the independent variable, time. This is precisely the quantity that one is attempting to evaluate from the kinetic data.

The appearance of the integral plot in Figure 34 is exactly what is expected if the drift in the tabular values of  $k_2$  is attributable to a constant determinate error in  $x/a_0(a_0 - x)$ . The intercept at the ordinate is positive, indicative of a positive contribution of the determinate error to Y. The source of the error was identified as a significant extent of reaction at low temperature before time zero, the time when the temperature of the reaction mixture was brought to 60°C. In this event, the initial concentration of the reactants ( $a_0$ ), and the concentrations of reactants

consumed at any given time ( $x$ ) are both too large by a constant amount corresponding to the extent of reaction before time zero. A constant error of this type makes a constant positive contribution to  $Y$ , and consequently a constant upward displacement of each data point is observed in Figure 34. Thus, the nature of Figure 34 is exactly as expected for second order kinetics over the range investigated if some reaction occurred before time zero. Likewise, the drift in the values for  $k_2$  calculated by the tabular method conform to the same type of error. Although the error in  $Y$  is constant, the error in  $Y/t$  is not, since  $t$  varies. As  $t$  increases, the influence of the error decreases, and the tabular values of  $k_2$  continually decline.

Table 24 lists the data required to calculate values of  $Y$  and  $Y/t$  for each data point. Two methods of calculation for  $Y$  and  $Y/t$  were employed. In the first of these, the effects of the determinate error were ignored. The results are those presented in Table 8 and Figure 34. In the second method (modified procedure), the concentration terms were compensated for the extent of reaction that occurred before time zero.

The magnitude of the determinate error was determined independently of the statistical treatment of the data by integration of the  $^1\text{H}$  nmr spectrum in Figure 53. The relative area of the peak at 118 Hz provided a measurement of the extent of reaction (6.9 %, 0.035 M) that occurred before heating, since this resonance was identified as that of super-

Table 24  
Kinetic Data for the Second Order Rate Constant  
for Bis(4-methylpyridine)boronium Iodide Formation

Sample	Time, secx10 <sup>-4</sup>	Unmodified Procedure				Modified Procedure			
		a <sub>O</sub>	x	a <sub>O</sub> -x	y <sup>a</sup>	a <sub>O</sub>	x	a <sub>O</sub> -x	y <sup>b</sup>
1	0.180	0.500	0.067	0.433	0.310	0.465	0.032	0.433	0.159
2	0.360	0.500	0.085	0.415	0.410	0.465	0.050	0.415	0.260
3	0.580	0.500	0.120	0.380	0.631	0.465	0.085	0.380	0.481
4	0.750	0.500	0.134	0.366	0.732	0.465	0.099	0.366	0.581
5	1.22	0.500	0.187	0.313	1.19	0.465	0.152	0.313	1.04
6	1.98	0.500	0.229	0.271	1.69	0.465	0.194	0.271	1.54
7	4.23	0.500	0.319	0.181	3.52	0.465	0.284	0.181	3.37
8	6.82	0.500	0.374	0.126	5.94	0.465	0.339	0.126	5.79
									0.15
									0.15
									0.15
									0.15
									0.15
									0.15
									0.15

<sup>a</sup> The results are presented in Figure 34

<sup>b</sup> The results are presented in Figure 36

saturated bis(4-methylpyridine)boronium iodide, a product of the reaction. To compensate for the extent of reaction that occurred before time zero, the initial concentrations of the reactants were adjusted to  $0.500 - 0.035 = 0.465$  M. Similar adjustments were made for the concentrations of starting materials reacted (X) at each time t to the proper values relative to time zero.

Figure 36 is the integral plot of the data for the modified procedure. The last entry in Table 24 ( $\Delta Y$ ) is the difference in the values of Y for the modified and unmodified procedure for each data point. It is notable that the value of  $\Delta Y$  is the same for each data point. Thus, it is apparent that the influence of a certain extent of reaction before time zero is, in fact, a constant positive error in Y. Thus, the slopes of Figures 34 and 36 are identical. The only difference between the plots is the upward displacement of each data point by a constant amount in the former. The effect of this displacement is reflected in the difference in the Y-intercepts for the two plots. The plot in Figure 36 passes through the origin, whereas that in Figure 34 has a positive Y-intercept.

It is significant that the intercept of the least squares plot was corrected to the origin by the use of an experimentally derived quantity for the constant determinate error. The same error is predicted by the intercept of Figure 34. The agreement between the two independently derived values for

the determinate error indicates that the assignments of the nature and source of the error were correct. Thus, the conclusion that second order kinetics are observed over the extent of reaction investigated is valid.

This conclusion is supported by a comparison of the tabular values calculated for the second order rate constant by the modified and unmodified procedures ( $k_2'$  and  $k_2$  respectively, in Table 8). After compensation for the determinate error, the calculated values of the second order rate constant ( $k_2'$ ) are in good agreement for each data point ( $S_r = 5.84 \%$ ) exhibiting only the scatter expected for randomized indeterminate errors.

Although it is possible to correct tabular calculations for a determinate error of the type encountered here once the error has been evaluated, it is doubtful that the error would have been recognized by use of the tabular method alone. The drift in the calculated values of  $k_2$  recorded in Table 8 suggest that second order kinetics were not followed over the reaction range examined. Further, a reliable value of the rate constant could not be readily ascertained from these data. By contrast, the determinate error was apparent when the data were evaluated graphically, and compliance with second order kinetics and a value of the rate constant over the reaction range investigated could be ascertained without any knowledge of the source of the error. Thus, the basic superiority of the graphical method for kinetic analysis is

apparent, and this method was employed whenever possible in this study.



# BIBLIOGRAPHY

1. J. C. Lockhart, Chem. Rev., 65, 131 (1965).
2. K. Moedritzer and W. J. Considine, Ann. N. Y. Acad. Sci., 159, 1 (1969).
3. J. C. Lockhart, Redistribution Reactions, New York: Academic Press, 1970.
4. H. A. Skinner, Rec. Trav. Chim., 73, 991 (1954).
5. J. R. Van Wazer, Ann. N. Y. Acad. Sci., 159, 5 (1969).
6. R. Koster, Ann. N. Y. Acad. Sci., 159, 5 (1969).
7. D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, Inorg. Chem., 8, 594 (1969).
8. M. F. Lappert, M. R. Litzow, J. B. Pedley, and T. R. Spalding, J. Chem. Soc. A, 383 (1971)
9. O. T. Beachley, Jr. and B. Washburn, Inorg. Chem., 14, 120 (1975).
10. G. A. Anderson and J. J. Lagowski, Inorg. Chem., 10, 1910 (1971).
11. J. W. Wiggins and G. E. Ryschkewitsch, Inorg. Chim. Acta, 4, 33 (1969).
12. A. G. Massey, Advan. Inorg. Chem. Radiochem., 10, 1 (1967).
13. J. S. Hartman and G. J. Schrobilgen, Inorg. Chem., 11, 940 (1972).
14. B. W. Benton and J. M. Miller, Can. J. Chem., 52, 2866 (1974).
15. R. J. Gillespie and J. S. Hartman, Can. J. Chem., 46, 2147 (1968).
16. J. S. Hartman and J. M. Miller, Inorg. Nucl. Chem. Lett., 5, 831 (1969).

17. J. M. Van Paasschen and R. A. Geanangel, Inorg. Nucl. Chem. Lett., 8, 879 (1972).
18. T. D. Coyle, Proc. Chem. Soc. London, 172, (1963).
19. H. Noeth and H. Beyer, Chem. Ber., 93, 2251 (1960).
20. M. J. Bula, D. E. Hamilton, and J. S. Hartman, J. Chem. Soc., Dalton, 1405 (1972).
21. B. Benton-Jones and J. M. Miller, Inorg. Nucl. Chem. Lett., 8, 485 (1972).
22. B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Kalsen, and J. M. Miller, J. Chem. Soc., Dalton, 2603 (1972).
23. S. S. Krishnamurthy and M. F. Lappert, Inorg. Nucl. Chem. Lett., 7, 919 (1971).
24. M. J. Bula and J. S. Hartman, J. Chem. Soc., Dalton, 1047 (1973).
25. M. J. Bula, J. S. Hartman, and C. V. Raman, J. Chem. Soc., Dalton, 725 (1974).
26. J. E. Drake and J. Simpson, J. Chem. Soc. A, 974 (1968).
27. J. E. Drake and B. Rapp, J. Chem. Soc., Dalton, 2341 (1972).
28. J. N. G. Faulks, N. N. Greenwood, and J. H. Morris, J. Inorg. Nucl. Chem., 29, 329 (1967).
29. J. R. Blackburn, J. Chem. Soc., Dalton, 2139 (1973).
30. N. N. Greenwood and K. Wade, J. Chem. Soc., 1130 (1960).
31. C. D. Schmulbach and I. Y. Ahmed, Inorg. Chem., 8, 1414 (1969).
32. I. Y. Ahmed and C. D. Schmulbach, Inorg. Chem., 8, 1411 (1969).
33. I. Y. Ahmed and C. D. Schmulbach, Inorg. Chem., 11, 228 (1972).
34. O. T. Beachley, Inorg. Chem., 4, 1823 (1965).
35. E. Mayer, Inorg. Chem., 11, 866 (1972).
36. S. G. Shore and C. L. Hall, J. Amer. Chem. Soc., 88, 5346 (1966).

37. M. Inone and G. Kodama, Inorg. Chem., 7, 430 (1968).
38. S. G. Shore and R. W. Parry, J. Amer. Chem. Soc., 80, 8 (1958).
39. H. Noeth, H. Beyer, and H. J. Vetter, Chem. Ber., 97 110 (1964).
40. W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Engelwood Cliffs, N. J.: Prentice-Hall, Inc., 1970, 492.
41. H. C. Brown and L. Domash, J. Amer. Chem. Soc., 78, 5385 (1956).
42. K. C. Nainan and G. E. Ryschkewitsch, Inorg. Chem., 8, 2671 (1969).
43. R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, J. Amer. Chem. Soc., 85, 487 (1963).
44. G. E. Ryschkewitsch and J. W. Wiggins, Inorg. Syn., 12, 116 (1970).
45. M. A. Mathur, S. Chandra, V. R. Miller, and G. E. Ryschkewitsch, in preparation.
46. S. Ratajczak, Bull. Soc. Chim. Fr., 487 (1960).
47. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 82, 3290 (1960).
48. J. R. Lowe, S. S. Uppal, C. Weidig, and H. C. Kelly, Inorg. Chem., 9, 1423 (1970).
49. G. E. Ryschkewitsch and J. M. Garrett, J. Amer. Chem. Soc., 89, 4240 (1967).
50. K. C. Nainan and G. E. Ryschkewitsch, Inorg. Chem., 7, 1316 (1968).
51. J. P. Wibault and F. W. Broekman, Rec. Trav. Chim., 52, 885 (1939).
52. K. C. Nainan and G. E. Ryschkewitsch, J. Amer. Chem. Soc., 91, 330 (1969).
53. I. Shapiro, C. O. Wilson, J. F. Ditten, and W. J. Lehmann, Advan. Chem. Ser., 32 127 and 139 (1961).
54. J. A. Bigot, T. J. De Boer, and F. L. J. Sixma, Rec. Trav. Chim., 76, 996 (1957).

55. D. Cook, Can. J. Chem., 42, 2523 (1964).
56. K. C. Nainan, unpublished data.
57. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, New York: McGraw-Hill Book Company, 1959, chap. 10.
58. A. Fischer, W. J. Galloway, and J. Vaughan, J. Chem. Soc., 3591 (1964).
59. H. C. Brown and X. R. Mihm, J. Amer. Chem. Soc., 77, 1723 (1955).
60. G. F. Lanthier and J. M. Miller, J. Chem. Soc. A, 346 (1971).
61. T. D. Coyle and F. G. A. Stone, Progress in Boron Chemistry, 1, 118 (1964).
62. W. H. Meyers, Doctoral Dissertation, University of Florida, 1972.
63. H. C. Brown and L. Domash, J. Amer. Chem. Soc., 78, 5384 (1956).
64. B. M. Mikhailov, Russ. Chem. Rev., 31, 207 (1962).
65. G. E. Ryschkewitsch and E. R. Birnbaum, Inorg. Chem., 4, 575 (1965).
66. H. C. Brown and R. R. Holmes, J. Amer. Chem. Soc., 77, 1727 (1955).
67. H. C. Brown, D. Gintis, and L. Domash, J. Amer. Chem. Soc., 78, 5387 (1956).
68. H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, J. Amer. Chem. Soc., 75, 1-24 (1953).
69. K. J. Laidler, Chemical Kinetics, New York: McGraw-Hill Book Company, 1965, chap. 1.
70. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1965, 69.
71. J. Fogelman and J. M. Miller, Can. J. Chem., 50, 1262 (1972).
72. W. W. Lochmaier, Doctoral Dissertation, University of Florida, 1969.

73. J. Y. Corey and R. West, J. Amer. Chem. Soc., 85, 2430 (1963).
74. N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, Inorg. Chem., 8, 862 (1969).
75. D. L. Reznicek and N. E. Miller, Inorg. Chem., 11, 858 (1972).
76. H. I. Schliesinger and A. B. Burg, Chem. Rev., 31, 1 (1942).
77. S. Matsumura and N. Tokura, Tetrahedron Lett., 4703 (1968).
78. E. L. Muetterties, The Chemistry of Boron and Its Compounds, New York: John Wiley and Sons, Inc., 1967, 234.
79. G. E. Ryschkewitsch, "Boron Cations," in Boron Hydride Chemistry, New York: Academic Press, 1975, chap. 6.
80. D. F. Gaines, Inorg. Chem., 2, 523 (1963).
81. H. C. Brown, P. F. Stehle, and P. A. Tierney, J. Amer. Chem. Soc., 79, 2020 (1957).
82. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Ithaca, N. Y.: Cornell University Press, 1953, 403.
83. R. E. Dessy and F. Paulik, J. Chem. Educ., 40, 185 (1963).
84. M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, J. Chem. Soc., 899 (1965).
85. S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, J. Amer. Chem. Soc., 78, 328 (1956).
86. H. Weiner and R. A. Sneen, J. Amer. Chem. Soc., 87, 292 (1965).
87. R. A. Sneen and J. W. Larsen, J. Amer. Chem. Soc., 88, 2594 (1966).
89. E. M. Kosower, "Charge-Transfer Complexing of Pyridinium Rings," in The Enzymes, vol. 3, New York: Academic Press, 1960, chap. 13.
90. E. M. Kosower and J. A. Skorcz, J. Amer. Chem. Soc., 82, 2195 (1960).
91. E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, J. Amer. Chem. Soc., 82, 2188 (1960).

92. D. L. King and D. R. Herschbach, Disc. Faraday Soc., 55, 331 (1973).
93. G. E. Ryschkewitsch, J. Amer. Chem. Soc., 89, 3145 (1967).
94. K. Hedborg and V. Schomaker, J. Amer. Chem. Soc., 73, 1482 (1951).
95. M. F. Hawthorne and E. S. Lewis, J. Amer. Chem. Soc., 80, 4296 (1958).
96. K. Wiberg, Chem. Rev., 55, 713 (1955).
97. R. Breslow, Organic Reaction Mechanisms, New York: W. A. Benjamin, Inc., 1966, 75.
98. K. C. Nainan and G. E. Ryschkewitsch, J. Amer. Chem. Soc., 91, 330 (1969).
99. G. S. Heaton and P. N. K. Riley, J. Chem. Soc. A, 952 (1966).
100. G. E. Ryschkewitsch and J. W. Wiggins, J. Amer. Chem. Soc., 92, 1790 (1970).
101. G. E. Ryschkewitsch and V. R. Miller, J. Amer. Chem. Soc., 95, 2836 (1973).
102. S. Brownstein and J. Paasivirta, Can. J. Chem., 43, 1645 (1965).
103. P. J. Burchill, S. Brownstein, and A. M. Eastham, Can. J. Chem., 45, 17 (1967).
104. W. J. Youden, Statistical Methods for Chemists, New York: John Wiley and Sons, Inc., 1964, chap. 5.
105. S. A. Fridmann and T. P. Fehlner, J. Phys. Chem., 75, 2711 (1971).
106. F. T. Smith and G. B. Kistiakowsky, J. Chem. Phys., 31, 621 (1959).
107. P. S. Ganguli and H. A. McGee, Jr., J. Chem. Phys., 50, 4658 (1969).
108. J. H. Wilson and H. A. McGee, Jr., J. Chem. Phys., 46, 1444 (1967).
109. M. E. Garabedian and S. W. Benson, J. Amer. Chem. Soc., 86, 176 (1964).

110. T. P. Fehlner and W. S. Koski, J. Amer. Chem. Soc., 87, 409 (1965).
111. W. L. Budde and M. F. Hawthorne, J. Amer. Chem. Soc., 93, 3147 (1971).
112. J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, New York: McGraw-Hill Book Company, 1968, 204 and 293.
113. L. Manziek, unpublished data.
114. R. C. Weast, Handbook of Chemistry and Physics, 50th Edition, New York: The Chemical Rubber Company, 1970, D-115.
115. G. E. Ryschkewitsch, unpublished data.
116. N. E. Miller and E. L. Muetterties, J. Amer. Chem. Soc., 86, 1033 (1964).
117. D. Skoog and D. M. West, Fundamentals of Analytical Chemistry, New York: Holt, Rinehart, and Winston, 1963, 53.
118. M. Ezekiel, Methods of Correlation Analysis, New York: John Wiley and Sons, Inc., 1941, 136.

## BIOGRAPHICAL SKETCH

Bruce Neil McMaster was born on January 19, 1945 in Salem, New Jersey, to Edward and Edna McMaster. He spent most of his childhood in Wilmington, Delaware, graduating from John Dickinson High School in 1963.

Mr. McMaster graduated from the University of Delaware in Newark, Delaware in 1968 with a B.S. in Chemistry. He entered the Graduate School at the University of Florida in the fall of 1968.

He was the recipient of two teaching excellence awards from the Phillips Petroleum Company and the duPont Company for his teaching as a graduate assistant from 1968-1970. He also was awarded an interim instructorship for the 1969-1970 academic year. Mr. McMaster was the recipient of a National Science Foundation Traineeship and a National Defense Education Act Title IV Fellowship.

Mr. McMaster is currently employed as an instructor in Chemistry at Sante Fe Community College, Gainesville, Florida, where he has been teaching since the fall of 1975.

Mr. McMaster is married to the former Joan Patricia Kennedy. Mr. and Ms. McMaster have one son, Darren, age 5.

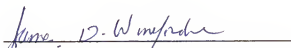


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Professor of Chemistry

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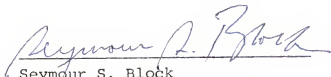
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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